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PAPER

Effective 1,5-, 1,6- and 1,7-remote stereocontrol in reactions of alkoxy- and hydroxy-substituted allylstannanes with aldehydes†

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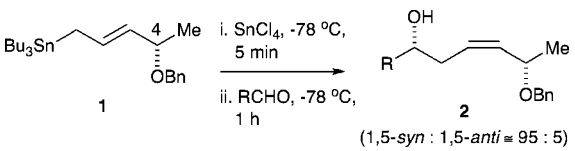
Alk-2-enylstannanes with 4-, 5- and 6-alkoxy- or -hydroxy-substituents are transmetallated stereoselectively with tin(IV) halides to generate allyltin trihalides which react with aldehydes to give (*Z*)-alk-3-enols with useful levels of 1,5-, 1,6- and 1,7-stereocontrol. Alk-2-enylstannanes with a stereogenic centre bearing a hydroxy or alkoxy group at the 4-, 5- or 6-position, react with overall (*Z*)-1,5-, 1,6- and 1,7-*syn*-stereoselectivity with respect to the hydroxy and alkoxy substituents. The analogous reactions of alkoxy- and -hydroxyalk-2-enylstannanes with a methyl bearing stereogenic centre at the 4- or 5-position react with overall (*Z*)-1,5- and 1,6-*anti*-stereoselectivity with respect to the hydroxy and methyl substituents.

Introduction

4-Benzyloxypent-2-enylstannane **1** is transmetallated by tin(IV) chloride to generate an allyltin trichloride which reacts with aldehydes to give the (*Z*)-1,5-*syn*-5-benzyloxyalk-3-en-1-ols **2** with excellent 1,5-stereocontrol.[1] This stereoselectivity usually dominates the intrinsic stereochemical bias of a chiral aldehyde and iterative reactions using an octa-2,7-dienylstannane have been used to prepare aliphatic 1,5,9,13-polyols and ethers with useful stereoselectivity.[2]



It was of interest to see whether remote stereocontrol was also observed for tin(IV) halide mediated reactions of alk-2-enylstannanes which had alkoxy and hydroxy substituents at the 5- and 6-positions. We now report full details of the 1,5- and 1,6-stereocontrol observed in the tin(IV) halide promoted reactions between aldehydes and the 5-alkoxy(hydroxy)alk-2-enylstannanes **I** and **II**, and 1,5-, 1,6- and 1,7-stereocontrol found for the analogous reactions with aldehydes of the 6-alkoxy(hydroxy)alk-2-enylstannanes **III–V**, see Fig. 1.[3,4]

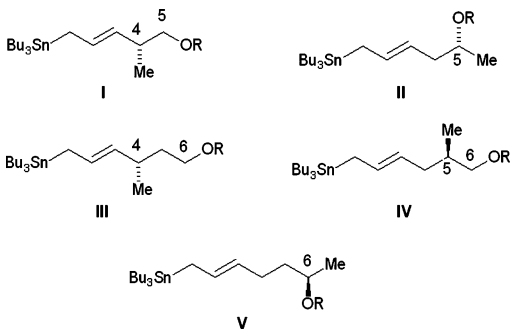


Fig. 1 Alk-2-enylstannanes selected for study.

Results and discussion

1,5-Stereocontrol using 5-alkoxyalk-2-enylstannanes I

The (*R*)-5-benzyloxy-4-methylpent-2-enylstannane **6** was synthesized as outlined in Scheme 1. Treatment of (*R*)-5-benzyloxy-4-methylpent-2-enol (**3**)[5] (e.e. >85%, Mosher's), an 80 : 20 mixture of (*E*)- and (*Z*)-isomers, with sodium hydride, carbon disulfide and methyl iodide gave the xanthate **4**. This on heating in toluene under reflux isomerised to give a 50 : 50 mixture of the epimeric dithiocarbonates **5**, which were converted into the 5-benzyloxypent-2-enylstannane **6**, as an 80 : 20 mixture of (*E*)- and (*Z*)-isomers, by heating with tributyltin hydride in benzene under free radical conditions.

Tin(IV) chloride was added to the mixture of (*E*)- and (*Z*)-isomers of the alkenylstannane **6** in dichloromethane at −78 °C to effect transmetallation. After 10 min, benzaldehyde was added and after a further hour the reaction was worked up to give a mixture of the 1,5-*anti*- and 1,5-*syn*-(*Z*)-hex-3-en-1-ols **7** and **8** in a ratio of 96 : 4, see Scheme 2. (*E*)-Alk-3-enols were not isolated and were only very minor products (<2%).

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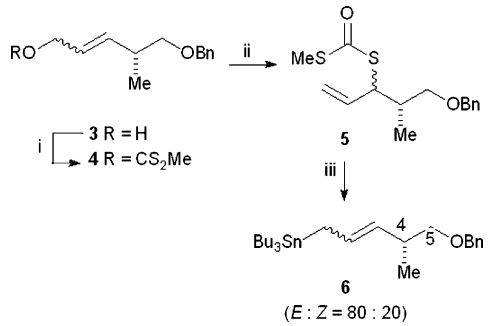
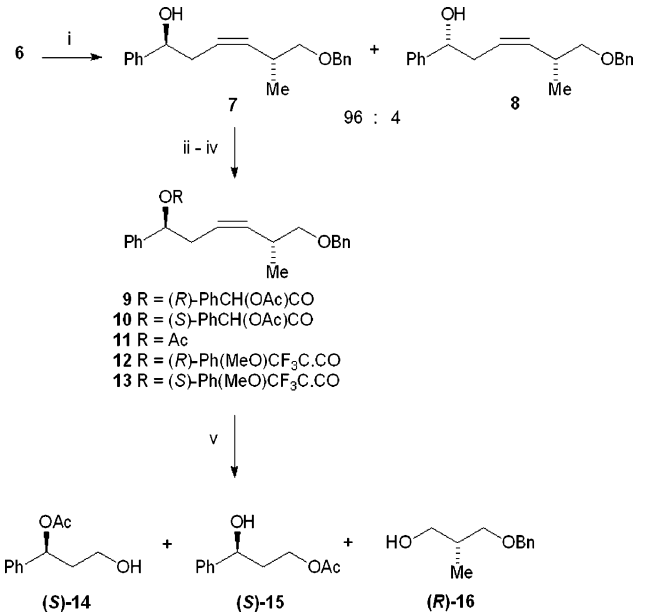
† Electronic supplementary information (ESI) available: full experimental details for the chemistry outlined in Schemes 3, 4, 5, 8, 10, 11, 12, 17, and 18 and all compounds listed in Table 1–6 together with copies of representative ^{1}H and ^{13}C NMR spectra. See DOI: 10.1039/c0ob01084g



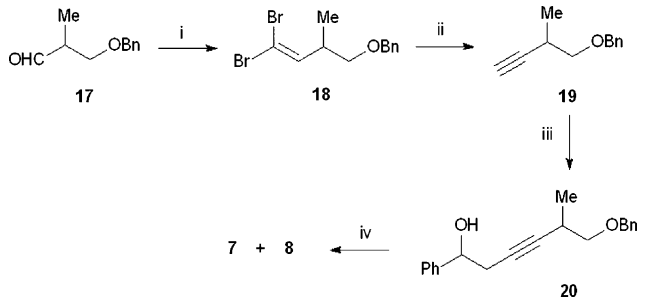
Scheme 1 Preparation of stannane **6**. Reagents and conditions: i, NaH, r.t., 1 h, CS_2, r.t., 3 h, then MeI, r.t. 15 h [76%; (*E*) : (*Z*) = 80 : 20]; ii, heat in toluene, 15 h (*ca*. 100%; 50 : 50 mixture); iii, Bu_3SnH, AIBN (trace), benzene, heat, 2.5 h [86%; (*E*) : (*Z*) = 80 : 20].



Scheme 2 Tin(IV) chloride mediated reaction of stannane **6** with benzaldehyde. Reagents and conditions: i, $SnCl_4$, −78 °C, 10 min, then PhCHO, 1 h (83%; **7** : **8** = 96 : 4); ii, (*R*)- or (*S*)-*O*-acetyl-mandelic acid, DCC, DMAP (cat), DCM, r.t., 15 h (**9**, 83%; **10**, 88%); iii, Ac_2O, DMAP (cat), Et_3N, DCM, r.t., 50 h (89%); iv, (*S*)- or (*R*)-Mosher's acid chloride, py., CCl_4, r.t. (**12**, 86%; **13**, 51%); v, O_3, $CHCl_3$, −60 °C, 30 min, DMS, r.t., then $NaBH_4$, MeOH, r.t., 3 h [(***S***)-**14**, 29%].

The major and minor products **7** and **8** could be distinguished by ^{1}H NMR, their ratio being estimated by integration of the doublets at δ0.91 and 0.95 attributed to their 5-CH_3 groups. To confirm that the two products were the epimers **7** and **8**, a mixture was prepared by reacting racemic styrene oxide with the racemic alkyne **19**,[6] which was available in two steps from 3-benzyloxy-2-methylpropanal **17**, see Scheme 3. This gave the hex-3-ynol **20** as a mixture of diastereoisomers and hydrogenation using Lindlar's catalyst gave a 50 : 50 mixture of the epimeric alcohols **7** and **8**. Comparison with the products from the tin(IV) chloride mediated reaction of stannane **6** with benzaldehyde confirmed that the (*Z*)-1,5-*syn*-epimer **8** was the minor product.

The 3,4-vinylic coupling constant of the major product **7** from the stannane reaction was 10 Hz consistent with the (*Z*)-geometry. The 1,5-*anti*-configuration was assigned by comparison of the ^{1}H NMR spectra of the (*R*)- and (*S*)-acetylmandelates **9** and **10**[7,8] and was confirmed by ozonolysis of the acetate **11** with a reductive work-up, which gave the (*S*)-3-acetoxy-3-phenylpropanol (*S*)-**14**, $[\alpha]_D$ −79 (*c* 0.61 in $CHCl_3$)[1a,9] and a mixture of the primary acetate (*S*)-**15**, formed by 1,3-migration of the acetyl group, and 3-benzyloxy-2-methylpropanol (*R*)-**16**, derived from the other fragment of the ozonolysis. The ^{19}F NMR spectra of the Mosher's derivatives **12** and **13** showed two products, in a ratio of *ca.* 91 : 9, the discrepancy from the 96 : 4 ratio of epimers **7** and **8** as estimated by ^{1}H NMR being attributed to the e.e. of 85% of the alkenylstannane **6** (*cf*. the e.e. of alcohol **3**).



Scheme 3 Synthesis of a mixture of the epimeric alcohols **7** and **8**. Reagents and conditions: i, CBr_4, Ph_3P, Zn powder, DCM, r.t., 24 h, then add **17**, r.t., 2.5 h (74%); ii, *n*-BuLi in hexane, −78 °C, 2 h, then r.t., 1 h (65%); iii, **19**, *n*-BuLi, THF, −78 °C, 20 min, BF_3. Et_2O, −78 °C, 20 min, add styrene oxide, −78 °C, 1.5 h (14%); iv, Lindlar's cat., H_2, r.t., 72 h (72%, a 50 : 50 mixture of **7** and **8**).

Tin(IV) chloride mediated reactions of allylstannane **6** with several aldehydes were investigated and the results are shown in Table 1. In all cases, useful diastereoselectivities in favour of the (*Z*)-1,5-*anti*-products were observed even for reactions of the stannane with enantiomeric chiral aldehydes. ^{1}H NMR confirmed the (*Z*)-configuration of the double-bonds of the major products and the diastereoselectivities of the reactions of the stannane with 4-methoxy- and 4-chloro-benzaldehyde.

Table 1 1,5-Stereocontrol in tin(IV) chloride mediated reactions between aldehydes and allylstannane **6**

R	1,5-*anti*-product[a]	Yield (%)	1,2-*anti* : 1,5-*syn*
Ph	**7**	83	96 : 4
4-$MeOC_6H_4$	**21**	65	96 : 4[b]
4-ClC_6H_4	**22**	67	96 : 4[c]
Me_2CH	**23**	80	95 : 5[d]
Et	**24**	69	95 : 5[b]
	**25**	70	95 : 5[d]
	**26**	73	95 : 5[d]

[a] In all cases, the vicinal ^{1}H NMR vinylic coupling constant was *ca*. 10 Hz. [b] Ratio by ^{1}H NMR and from Mosher's derivatives; configuration by analogy. [c] Ratio by ^{1}H NMR; configuration by analogy. [d] Ratio by ^{1}H NMR and/or Mosher's; configuration assigned using *O*-acetylmandelates.

The ^{19}F spectra of the Mosher's derivatives of the product **21** from 4-methoxybenzaldehyde were also consistent with the 1,5-*anti*-configuration. Configurations were assigned to the major products **23**, **25** and **26** from 2-methylpropanal and (*R*)- and (*S*)-2-benzyloxypropanal by comparison of the ^{1}H NMR spectra of their *O*-acetylmandelates, and the ^{19}F spectra of their Mosher's derivatives, which also indicated the 1,5-stereoselectivity.

The minor product in each case was assigned the (*Z*)-1,5-*syn*-configuration by analogy with the formation of the (*Z*)-1,5-*syn*-isomer **8** in the reaction with benzaldehyde.

The use of other Lewis acids to promote reactions of allylstannane **6** with aldehydes was briefly investigated. With dibutyltin dichloride, titanium(IV) chloride, aluminium(III) chloride and boron trifluoride diethyletherate, complex mixtures of products were obtained. A modest, 40%, yield of the 1,5-*anti*- and 1,5-*syn*-products **7** and **8**, ratio 95 : 5, was obtained using butyltin trichloride. However, with tin(IV) bromide, improved 1,5-(*Z*)-*anti* : 1,5-(*Z*)-*syn* stereoselectivities of *ca.* 99 : 1 were obtained for reactions of the allylstannane **6** with the arylaldehydes, and improved stereoselectivities for reactions with 2-methylpropanal and propanal. No (*E*)-isomers of the products were detected in the product mixtures from these reactions.

The regio- and stereo-selectivities of these tin(IV) halide promoted reactions of stannane **6** with aldehydes are consistent with a kinetically controlled stereoselective intramolecular transmetallation, see Fig. 2. This generates the allyltin trihalide **28** in which the vinyl and methyl substituents are *trans*-disposed, *i.e.* pseudoequatorial, with respect to the 5-membered ring formed by co-ordination of the oxygen of the benzyloxy group with the electron deficient tin. The allyltin trihalide can then react with an aldehyde *via* the chair-like six-membered transition state, **29** in which the substituent next to the tin adopts the axial position to give the 1,5-*anti*-(*Z*)-products after an aqueous work-up.

To check the compatibility of this chemistry with a 2-alkyl substituent in the allylstannane, an (*E*,*Z*)-mixture of the 5-*tert*-butyldimethylsilyl-2,4-dimethylpent-2-enylstannane **33** was prepared, see Scheme 4. Thus the alcohol **30** (e.e. *ca.* 50%[11]) was converted into the xanthate **31**, which on heating underwent a

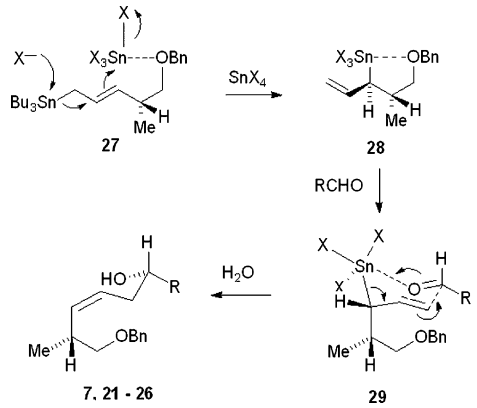


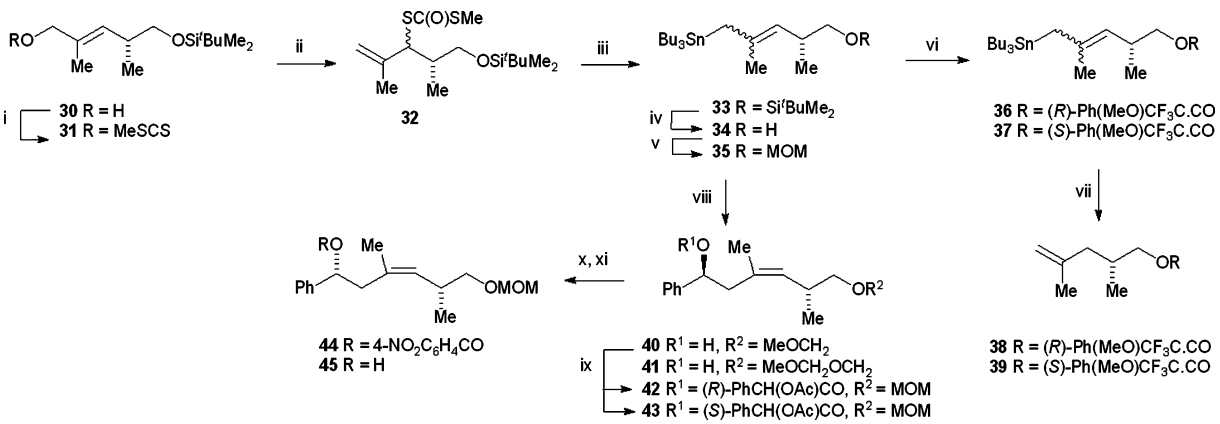
Fig. 2 Mechanism proposed to account for the stereoselectivity of tin(IV) halide promoted reactions of allylstannane **6** and aldehydes.

3,3-sigmatropic rearrangement to give the dithiocarbonate **32** as a 60 : 40 mixture of epimers. On reaction with tributyltin hydride under free radical conditions, these were converted into the stannane **33**. Following desilylation, *O*-alkylation of the resulting hydroxystannane **34** then gave the 5-(methoxymethoxy)pent-2-enylstannane **35**.

To check its optical purity, hydroxystannane **34** was converted into the Mosher's derivatives **36** and **37**, but the ^{19}F NMR spectra of these were complicated by the presence of geometrical isomers. However, protonolysis gave the pent-4-enyl esters **38** and **39**, which by ^{19}F NMR were estimated to have e.e.s of *ca.* 50%.

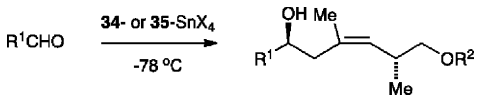
The tin(IV) chloride promoted reaction of the alk-2-enylstannane **35** with benzaldehyde proceeded with excellent stereoselectivity to give the 1,5-*anti*-(*Z*)-hex-3-en-1-ol **40** (69%). Just one minor side-product was isolated and was identified as the 6-(methoxymethoxymethoxy)hex-3-enol **41** (6%) attributed to traces of (methoxymethoxy)methyl chloride in the MOM-chloride used to prepare the stannnane **35**.

The (*Z*)-configuration of the major product **40** was confirmed by NOE, a significant enhancement of 4-H being observed on irradiation of the 3-CH_3. The configuration at C(1) was established



Scheme 4 Synthesis of 2,4-dimethylpent-2-enylstannanes and their reactions with benzaldehyde. Reagents and conditions: i, NaH, CS_2, MeI (94%); ii, heat in toluene, 18 h (75%; a 60 : 40 mixture of epimers); iii, Bu_3SnH, AIBN, benzene 3 h; iv, TBAF (88% from the dithiocarbonate **32**; a 55 : 45 mixture of geometric isomers); v, $MeOCH_2Cl$, $^{i}Pr_2NEt$ (79%); vi, (*S*)- or(*R*)-Mosher's acid chloride, py (**36**, 38%; **37**, 66%); vii, HBr, EtOH (87–93%); viii, $SnCl_4$, −78 °C, 10 min then PhCHO, −78 °C, 1 h (**40**, 69%, **41**, 6%); ix, (*R*)- or (*S*)-*O*-acetylmandelic acid, DCC, DMAP (**42** and **43**, both *ca.* 100%); x, 4-$NO_2C_6H_4CO_2H$, Ph_3P, DEAD (33%); xi, NaOH, MeOH (72%).

Table 2 1,5-Stereocontrol in tin(IV) halide mediated reactions between aldehydes and allylstannanes **34** and **35**



R^1	Stannane	SnX_4 (X)	1,5-*anti*-product[a]	R^2	Yield (%)	1,5-*anti* : 1,5-*syn*[a]
Ph	**35**	Cl	**40**	MOM	69	≥98 : 2
4-$MeOC_6H_4$	"	"	**46**	"	49	≥98 : 2
^{i}Pr	"	"	**47**	"	57	≥98 : 2
MeCH═CH	"	"	**48**	"	68	≥98 : 2
Ph	**34**	Br	**49**	H	92	≥98 : 2
MeCH═CH	"	"	**50**	"	89	≥98 : 2

[a] Ratio by ^{1}H NMR.

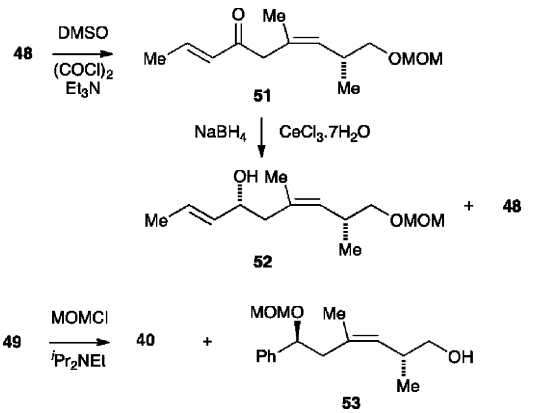
by comparison of the ^{1}H NMR chemical shifts of the *O*-acetylmandelates **42** and **43**.

To establish the stereoselectivity of this reaction, the 1,5-*anti*-product **40** was converted into its 1,5-*syn*-diastereoisomer **45** *via* a Mitsunobu reaction[12] followed by saponification of the inverted 4-nitrobenzoate **44**, see Scheme 4. Epimers **40** and **45** could be distinguished by NMR, for example, the doublet due to the 5-CH_3 group was seen at δ0.87 in the ^{1}H NMR spectrum of the 1,5-*anti*-product **40** and at δ1.03 in the ^{1}H NMR spectrum of the 1,5-*syn*-epimer **45**. The 1,5-*syn*-alkenol **45** was not detected in the product mixture from the reaction of allylstannane **35** with benzaldehyde, and so the 1,5-*anti* : 1,5-*syn* selectivity was estimated to be ≥98 : 2.

The tin(IV) chloride promoted reactions of the allylstannane **35** with methoxybenzaldehyde, 2-methylpropanal and (*E*)-but-2-enal were also highly stereoselective in favour of the (*Z*)-1,5-*anti*-alkenols **46–48**, see Table 2. Structures were assigned to these products by analogy with the stereoselective formation of the (*Z*)-1,5-alkenol **40** in the reaction with benzaldehyde. (*Z*)-1,5-*syn*-Epimers were not detected from these reactions but to check that 1,5-*anti*- and 1,5-*syn*-epimers could be distinguished, the (*Z*)-1,5-*anti*-product **48** from the reaction with (*E*)-but-2-enal was oxidised, and the resulting ketone **51** reduced to give a mixture of the epimeric alkenols **48** and **52**. These were clearly different by ^{1}H and ^{13}C NMR and the (*Z*)-1,5-*syn*-epimer **52** was not detected in the product mixture from the tin(IV) chloride promoted reaction of stannane **35** and (*E*)-but-2-enal. The only side-products isolated from these reactions were the minor 6-(methoxymethoxymethoxy)alk-3-en-1-ols due to the impurity in the MOM-protected stannane **35**.

The free hydroxystannane **34** was also found to react, after transmetallation with tin(IV) bromide, with benzaldehyde and (*E*)-but-2-enal to give the 1,5-*anti*-(*Z*)-alkenols **49** and **50** with excellent yields, 92 and 89% and diastereoselectivities, >99 : 1. The (*Z*)-1,5-*anti*-configuration assigned to the product **49** from the reaction of stannane **34** with benzaldehyde was confirmed by MOM-protection, which gave the known 1,5-*anti*-alkenol **40** together with a small amount of its regioisomer **53**. The structure of the product **50** was assigned by analogy.

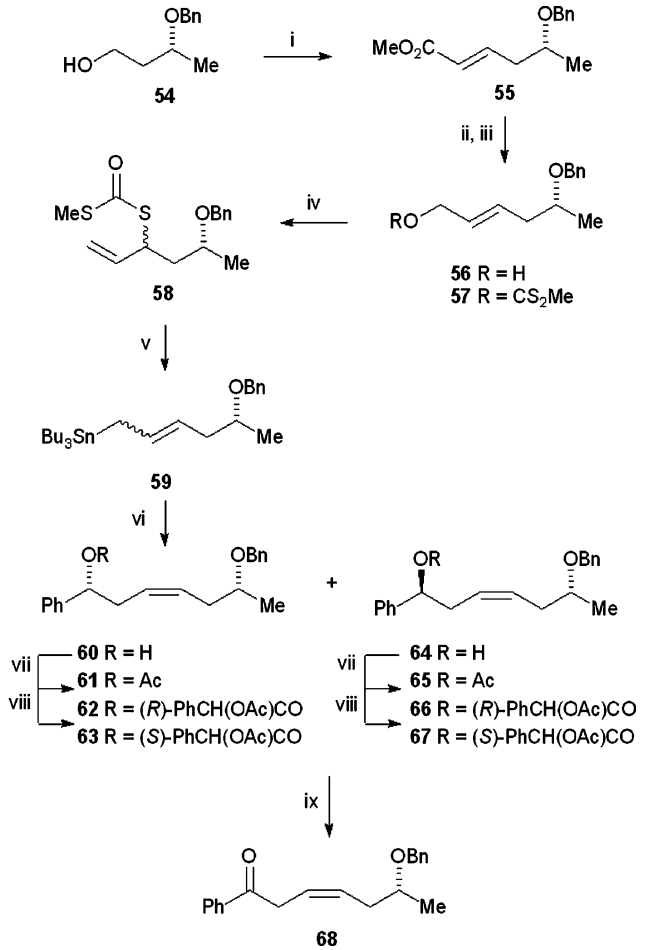
5-Alkoxy-4-methylpent-2-enyl(tributyl)stannanes, *cf*. generic structure **I**, appear to undergo highly stereoselective reactions with aldehydes on transmetallation with tin(IV) halides to give 1,5-*anti*-(*Z*)-alk-3-enols. This stereoselectivity, which can be promoted by either tin(IV) chloride or tin(IV) bromide, is compatible with an additional 2-methyl substituent, with different alkoxy substituents, and even with an unprotected 5-hydroxyl group in the stannane. The next phase of this work was to study analogous reactions of 5-substituted hexenylstannanes, *cf*. structure **II**, for 1,6-remote stereocontrol.



1,6-Stereocontrol using 5-substituted alkenylstannnanes II

The 5-benzyoxyhex-2-enylstannane **59** was synthesized to evaluate the ability of a 5-benzyloxy substituent to deliver 1,6-stereocontrol in reactions with aldehydes, see Scheme 5. (*R*)-3-Benzyloxybutanol **54** was converted into the 5-benzyloxyhex-2-enol **56** *via* oxidation,[13] a Wittig reaction to give the (*E*)-ester **55** together with 5% of its (*Z*)-isomer, and reduction. Heating the corresponding xanthate **57** gave the dithiocarbonate **58** which was converted into the stannane **59**, as a 2 : 1 mixture of (*E*)- and (*Z*)-isomers, by treatment with tributyltin hydride under free-radical conditions.

However, tin(IV) chloride and bromide promoted reactions of stannane **59** with benzaldehyde gave mixtures of the 1,6-*syn*- and 1,6-*anti*-products **60** and **64**. These products were shown to be epimers since oxidation of the mixture gave a single ketone **68**. Their configurations at C(1) were established by comparison of the ^{1}H NMR spectra of their (*R*)-and (*S*)-*O*-acetylmandelates **62/63** and **66/67**. The alkene geometry of the 1,6-*syn*-product **60** was established by the 3,4-vinylic coupling constant of *ca*. 10–11 Hz observed for the acetate **61** and the *O*-acetylmandelates **62** and **63**. The ^{1}H NMR spectrum of the (*S*)-*O*-acetylmandelate **67** also established the double-bond geometry of the *anti*-epimer **64**. Reasonable yields were obtained for these reactions, but the



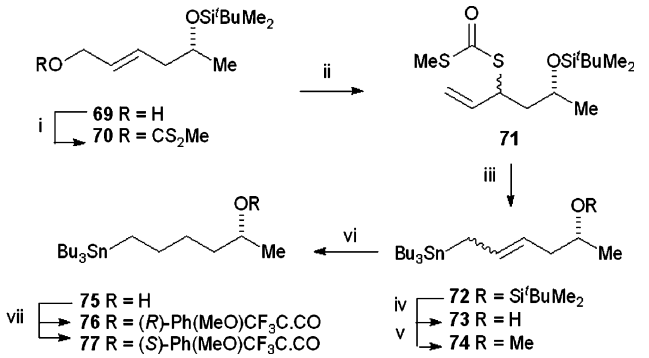
Scheme 5 Chemistry of the 5-benzyloxyhex-2-enylstannane **59**. Reagents and conditions: i, DMSO, $(COCl)_2$, DCM, −50 °C, 15 min, Et_3N, −50 °C, 5 min, r.t., 20 min, then $MeO_2C.CHPPh_3$, DCM, r.t., 15 h [70% plus 5% of its (*Z*)-isomer]; ii, DIBAL-H, hexane, DCM, −78 °C, 3 h (97%); iii, NaH, benzene, r.t., 1 h, CS_2, r.t., 3 h, MeI, r.t., 15 h (88%); iv, toluene, heat, 15 h (*ca.* 100%, 1 : 1); v, Bu_3SnH, AIBN (trace), benzene, heat, 3 h [67%; (*E*) : (*Z*) = 2 : 1]; vi, $SnCl_4$ or $SnBr_4$, −78 °C, 2–20 min, PhCHO, −78 °C, 1 h (44–76%); vii, Ac_2O, DMAP (cat), Et_3N, DCM, r.t., 15 h (**61**, 87%; **65**, 88%); viii, (*R*)- or (*S*)-*O*-acetylmandelic acid, DCC, DMAP (cat), DCM, r.t., 15 h (**62**, 82%; **63**, 77%; **66**, 80%; **67**, 87%); ix, DMSO, $(COCl)_2$, DCM, −50 °C, 15 min, $^iPr_2NEt$, −50 °C, 5 min (49%).

proportions of the two products varied, typically with only modest stereoselectivity in favour of the 1,6-*syn*-epimer **60**.

The *tert*-butyldimethylsilyloxyhex-2-enylstannane **72** was prepared to see whether stannanes analogous to the 5-benzyloxyhexenylstannane **59**, but with different *O*-substituents, reacted with aldehydes with better remote stereocontrol, see Scheme 6.

Xanthate **70**, available from the alcohol **69**, rearranged on heating to give the dithiocarbonate **71** as a mixture of epimers. Reaction with tributyltin hydride then gave the stannnane **72** as a 2 : 1 mixture of (*E*)- and (*Z*)-isomers. Desilylation was achieved using tetrabutylammonium fluoride to give the 5-hydroxyhex-2-enylstannane **73**, which was methylated to give the 5-methoxyhex-2-enylstannane **74**.

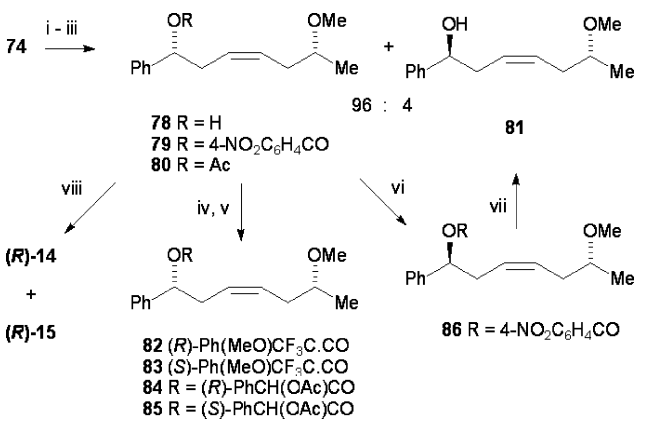
The optical purity of stannane **73** was checked by reduction using di-imide to give the 5-hydroxyhexylstannane **75**. This was



Scheme 6 Preparation of 5-hydroxyhex-2-enylstannane **73**. Reagents and conditions: i, NaH, benzene, 40 °C, 2 h, CS_2, r.t., 3 h, MeI, r.t., 15 h (92%); ii, toluene, heat, 15 h (*ca.* 100%, 1 : 1); iii, Bu_3SnH, AIBN (trace), benzene, heat, 3.5 h [85%, (*E*) : (*Z*) = 2 : 1]; iv, TBAF, THF, r.t., 15 h (88%); v, NaH, THF, 35 °C, 2 h, MeI, r.t., 15 h (85%); vi, $TsNHNH_2$, NaOAc, EtOH, heat, 4 h (83%); vii, (*S*)- or (*R*)-Mosher's acid chloride, py., r.t. 15 h (**76**, *ca.* 100%; **77**, 70%).

converted into its Mosher's derivatives **76** and **77**. A comparison of the ^{19}F NMR spectra of these confirmed that the e.e. of stannane **73** was >98%, see Scheme 6.

Transmetallation of the 5-methoxyhex-2-enylstannane **74** using tin(IV) bromide generated an allyltin tribromide, which reacted with benzaldehyde to give a mixture of the inseparable (*Z*)-1,6-*syn*- and (*Z*)-1,6-*anti*-6-methoxyhept-3-enols **78** and **81**, ratio 91 : 9, see Scheme 7. The use of tin(IV) chloride resulted in significantly lower stereoselectivity, **78** : **81** = 70 : 30. The major product was converted into the minor *via* a Mitsunobu reaction with inversion using 4-nitrobenzoic acid followed by saponification of the resulting ester **86**. The two alcohols were distinctly different by NMR and the product ratio from the allylstannane reaction could be measured by integration of peaks in its ^{13}C NMR spectrum. Interestingly the 4-nitrobenzoate **79** prepared by esterification of the major alcohol **78** and its epimer **86** from the Mitsunobu reaction, could not be

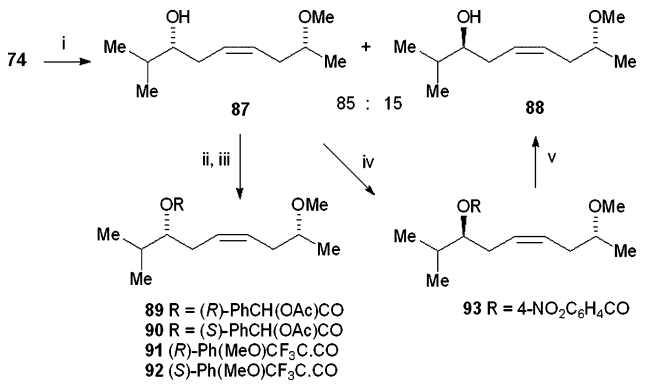


Scheme 7 1,6-Stereocontrol in the reaction of stannane **74** and benzaldehyde. Reagents and conditions; i, $SnBr_4$, DCM, −78 °C, 10 min, PhCHO, −78 °C, 1 h (78%; **78** : **81** = 91 : 9); ii, $O_2NC_6H_4COCl$, DMAP, Et_3N, DCM, r.t., 72 h (**79**, 88%); iii, Ac_2O, DMAP, Et_3N, DCM, r.t., 15 h (92%); iv, (*S*)- or (*R*)-Mosher's acid chloride, py (**82**, 97%; **83**, 78%); v, (*R*)- or (*S*)-*O*-acetylmandelic acid, DCC, DMAP, DCM, r.t. 15 h (**84**, 80%; **85**, 87%); vi, **78**, 4-$O_2NC_6H_4CO_2H$, Ph_3P, DEAD, tol, −35 °C to r.t., 2 h (80%); vii, NaOH, MeOH, r.t., 2 h (84%); viii, O_3, $CHCl_3$, −78 °C, 15 min, DMS, r.t., then $NaBH_4$, MeOH, DCM, r.t., 1.5 h [(*R*)-**14**, 58%; (*R*)-**15**, 15%].

distinguished by NMR. The high optical purity of the stannane, and hence of the products in this series, meant that the ratio of the epimers **78** and **81** could also be estimated using the ^{19}F spectra of the Mosher's derivatives **82** and **83**.

The 1,6-*syn*-configuration assigned to the major product **78** was established by ozonolysis of its acetate **80**, which gave (*R*)-3-acetoxy-3-phenylpropanol (*R*)-**14** together with the product (*R*)-**15** of acetate migration.[1a] Comparison of the ^1H NMR spectra of the (*R*)-and (*S*)-*O*-acetylmandelates **84** and **85** supported this assignment. The vinylic coupling constant of 11 Hz in the ^1H NMR spectra of the Mosher's derivatives **82** and **83** and the *O*-acetylmandelates **84** and **85** confirmed the (*Z*)-geometry of the alkene.

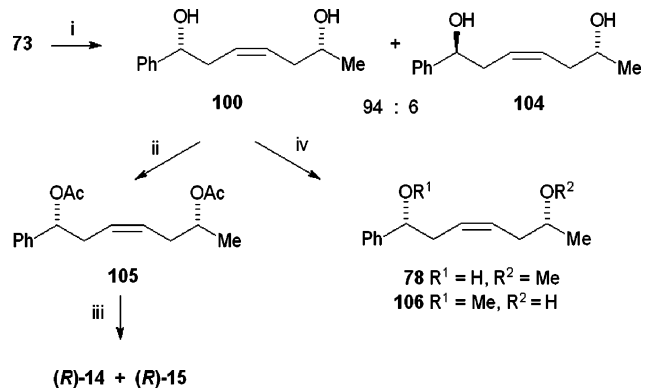
The tin(IV) bromide promoted reaction of the 5-methoxyhexenylstannane **74** with 2-methylpropanal was also stereoselective, the (*Z*)-3,8-*syn*-8-methoxynon-5-en-3-ol **87** being the major product, see Scheme 8. To check that the major and minor products were epimers, the major alkenol **87** was converted into the minor **88** using a Mitsunobu reaction followed by saponification of the resulting ester **93**. Minor differences were seen in the ^1H and ^{13}C NMR spectra of these epimers. The C(3) configuration of the major product **87** was established by comparison of the ^1H NMR data of *O*-acetylmandelates **89** and **90**. The reaction diastereoselectivity was estimated by ^{13}C NMR spectra of the product mixture and from the ^{19}F NMR spectra of the Mosher's derivatives **91** and **92**. The 10.5 Hz vinylic coupling constant in the ^1H NMR spectrum of the (*S*)-Mosher's derivative **92** confirmed the (*Z*)-geometry.



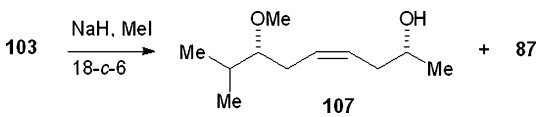
Scheme 8 1,6-Stereocontrol in the reaction of stannane **74** and 2-methylpropanal. Reagents and conditions: i, $SnBr_4$, −78 °C, 10 min, ^{i}PrCHO, −78 °C, 1 h (72%; **87**:**88** = 85:15); ii, (*R*)- or (*S*)-*O*-acetylmandelic acid, DCC, DMAP, DCM, r.t. 15 h (**89**, 81%; **90**, 51%); iii, (*S*)- or (*R*)-Mosher's acid chloride, py (**91**, 89%; **92**, 98%); iv, 4-$O_2NC_6H_4CO_2H$, Ph_3P, DEAD, tol, −35 °C to r.t., 18 h (45%); v, NaOH, MeOH, r.t., 2.5 h (92%).

Tin(IV) bromide promoted reactions of the 5-methoxyhexenylstannane **74** with other aldehydes were investigated, see Table 3. In all cases the (*Z*)-1,6-*syn*-isomers were the major products with useful stereoselectivity for achiral aldehydes. Matching and mismatching was observed for the chiral aldehydes, (*R*)- and (*S*)-2-benzyloxypropanal, with Felkin–Anh rather than chelation control being preferred. The structures of the products from these reactions were assigned by analogy with the products **78**/**81** and **87**/**88** from the reactions between alkenylstannane **74** and benzaldehyde or 2-methylpropanal. Mosher's derivatives and *O*-acetylmandelates were used to establish the reaction selectivities and the configurations of the hydroxyl bearing stereogenic centres in the products.

The 5-hydroxyhex-2-enylstannane **73** was also found to undergo stereoselective reactions with aldehydes in favour of (*Z*)-1,6-*syn*-products after transmetallation with tin(IV) halides. With benzaldehyde, a 90:10 mixture (59%) of the 1,6-*syn*- and 1,6-*anti*-epimers **100** and **104** was obtained using tin(IV) chloride, with a better yield (72%) and stereoselectivity, 94:6, being obtained using tin(IV) bromide, see Scheme 9. The ratios of the products **100** and **104** were determined by integration of the benzylic protons observed at δ4.68 for the 1,6-*syn*-epimer **100**, and at δ4.77 for the minor 1,6-*anti*-isomer **104**. The configuration of the major product **100** at the benzylic position, C(1), was established by ozonolysis of its bis-acetate **105** which, after reduction, gave the primary alcohol (*R*)-**14** (61%), together with the secondary alcohol (*R*)-**15** (13%).[1a] *O*-Methylation also gave a mixture of the regioisomeric monomethyl ethers **78** and **106**, the former being identical to the major product from the reaction of the 5-methoxyhex-2-enylstannane **74** with benzaldehyde. The minor product **104** was identified by analogy with earlier work.



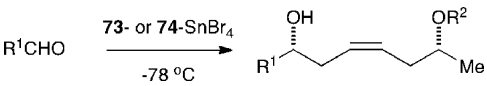
Scheme 9 1,6-Stereocontrol in the reaction of the 5-hydroxyhexenylstannane **73** and benzaldehyde. Reagents and conditions: i, SnX_4, −78 °C, 10 min, PhCHO, −78 °C, 1 h (with $SnCl_4$; 59%, **100**:**104** = 90:10; with $SnBr_4$, 72%, **100**:**104** = 94:6); ii, Ac_2O, Et_3N, DMAP, DCM, r.t., 15 h (91%); iii, O_3, $CHCl_3$, −78 °C, 15 min, DMS, r.t., then $NaBH_4$, MeOH, DCM, r.t., 15 min [(*R*)-**14**, 61%, (*R*)-**15**, 13%]; iv, NaH, 18-crown-6, THF, r.t., 15 min, diol **100**, r.t., 45 min, MeI, r.t., 15 h (**78**, 11%, **106**, 45%).



Tin(IV) bromide promoted reactions of the 5-hydroxyhex-2-enylstannane **73** and other aldehydes were investigated, see Table 3. In all cases useful levels of (*Z*)-1,6-*syn*-stereoselectivity were observed. The product ratios in these cases were determined by ^1H and ^{13}C NMR. The structure of the major product **103** from 2-methylpropanal was confirmed by *O*-methylation, which gave the regioisomeric monomethyl ethers **107** and **87**, the latter being identical to the major product from the reaction of 2-methylpropanal with the 5-methoxyhexenylstannane **74**.

The (*Z*)-1,6-*syn*-stereoselectivity observed for the tin(IV) bromide mediated reactions of the 5-hydroxy- and 5-methoxy-hex-2-enylstannanes **73** and **74** with aldehydes is consistent with participation of the allyltin tribromides **108** in which the vinyl

Table 3 1,6-Stereocontrol in tin(IV) bromide mediated reactions between aldehydes and allylstannanes **73** and **74**



R^1	Stannane	1,6-*syn*-product[a]	R^2	Yield (%)	1,6-*syn* : 1,6-*anti*
Ph	**74**	**78**	Me	78	96 : 4
4-$MeOC_6H_4$	"	**94**	"	65	93 : 7[b]
4-ClC_6H_4	"	**95**	"	61	92 : 8[b]
Me	"	**96**	"	69	91 : 9[c]
Et	"	**97**	"	67	84 : 16[b]
Me_2CH	"	**87**	"	72	85 : 15
	"	**98**	"	88	75 : 25[d]
	"	**99**	"	73	90 : 10[d]
Ph	**73**	**100**	H	72	94 : 6
4-$O_2NC_6H_4$	"	**101**	"	71	94 : 6[c]
Me	"	**102**	"	60	96 : 5[c]
Me_2CH	"	**103**	"	59	93 : 7

[a] In all cases the (*Z*)-configuration was confirmed by vicinal vinylic ^1H couplings of *ca.* 10 Hz observed either for the products or for a derivative of the products. [b] Ratio from ^1H NMR, ^{13}C NMR and Mosher's ^{19}F spectra; relative ^{19}F chemical shifts for the Mosher's derivatives were consistent with the 1,6-*syn*-configuration. [c] Ratio by ^1H and ^{13}C NMR; structure by analogy. [d] Ratio from ^1H NMR, ^{13}C NMR and Mosher's ^{19}F spectra; ^1H data of *O*-acetylmandelates and the relative ^{19}F chemical shifts for the Mosher's derivatives established the 1,6-*syn*-configuration.

and methyl groups are *cis*-disposed, *i.e.* pseudo-equatorial, about the five-membered ring formed by co-odination of the methoxy or hydroxy group with the electron deficient tin, see Fig. 3. Reaction of these allyltin tribromides with an aldehyde *via* the six-membered, chair-like transition state **109**, in which the group next to tin adopts the axial position, would then account for the overall (*Z*)-1,6-*syn*-stereocontrol. The use of tin(IV) bromide rather than tin(IV) chloride led to improved 1,6-*syn*-stereoselectivity in these reactions. Better stereoselectivity was also observed for the 5-hydroxy- and 5-methoxy-alkenylstannanes **73** and **74**, in comparison with that found for the 5-benzyloxyhexenylstannane **59**.

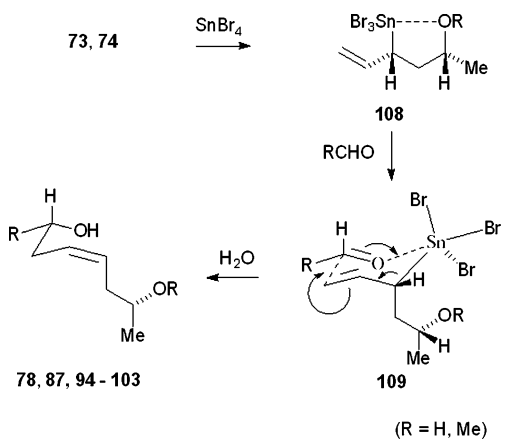
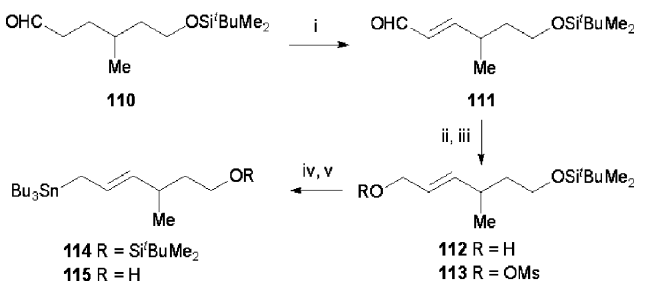


Fig. 3 Mechanism proposed to account for the 1,6-*syn*-stereoselectivity in reactions of allylstannanes **73** and **74** with aldehydes.

Having studied reactions of 5-alkoxy(hydroxyl)alk-2-enylstannanes for 1,5- and 1,6-stereocontrol, it was decided that 6-hydroxyalkenylstannanes should be studied, see generic structures **III**, **IV** and **V**, for 1,5-, 1,6- and 1,7-stereocontrol. Hydroxy substituted alkenylstannanes were selected for study, since the hydroxyl group had proved to be an effective co-ordinating group for 1,6-stereocontrol in 5-substituted systems.

1,5-Stereocontrol using 4-methyl-6-hydroxyhex-2-enylstannnane III (R = H)

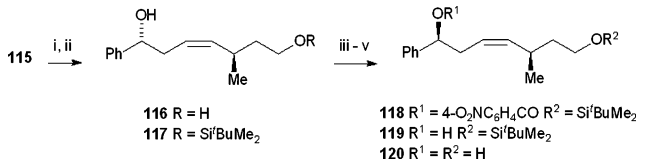
The racemic aldehyde **110** was available in two steps from citronellol[14] and was dehydrogenated to give the unsaturated aldehyde **111**, see Scheme 10.[15] Reduction gave the alcohol **112** which was converted to the stannane **114** by displacement of its mesylate **113**.[16] Desilylation then gave the racemic 6-hydroxy-4-methylhexenylstannane **115**.



Scheme 10 Synthesis of the racemic 6-hydroxy-4-methylhexenylstannane **115**. Reagents and conditions; i, $(EtO)_2P(O)OCH_2CH{=}CH_2$, $Pd(Ac)_2$, $NaHCO_3$, THF, heat, 72 h (95%); ii, DIBAL-H, THF, −78 °C to −45 °C, 3 h (84%); iii, MsCl, DCM, Et_3N, −7 °C, 10 min; iv, Bu_3SnLi, THF, −78 °C, 2 h, r.t., 15 h (53% from **112**); v, TBAF, THF, r.t., 15 h (72%).

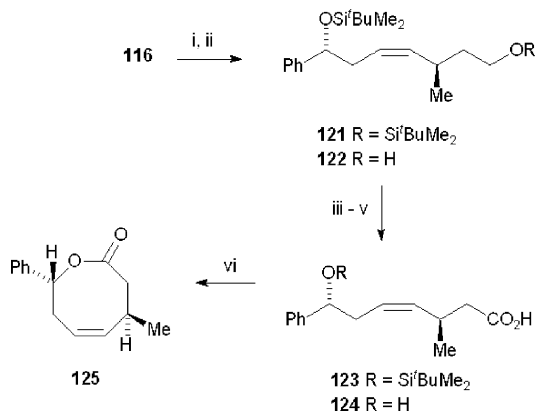
The reaction between the racemic 6-hydroxy-4-methylhex-2-enylstannane **115** and benzaldehyde mediated by tin(IV) bromide

gave the (*Z*)-1,5-*anti*-hept-3-ene-1,7-diol **116** (64%) with excellent stereoselectivity. With tin(IV) chloride, a lower yield, 40%, and slightly reduced stereoselectivity, 95 : 5, was observed. The *syn*-epimer **120** was prepared from diol **116** by selective silylation of the primary hydroxyl group and esterification of the secondary hydroxyl group of the resulting monosilyl ether **117** using a Mitsunobu reaction to give the inverted 4-nitrobenzoate **118**. Saponification and desilylation gave the inverted 1,5-*syn*-diol **120**, see Scheme 11. Epimers **116** and **120** could be distinguished by ^{1}H and ^{13}C NMR, and the 10.5 Hz vinylic coupling observed for the 1,5-*anti*-product **116** confirmed the (*Z*)-alkene geometry. Only traces of the 1,5-*syn*-epimer **120** were present in the product mixture from the allylstannane reaction.



Scheme 11 1,5-Stereocontrol in the reaction of 6-hydroxyhexenyl-stannane **115** and benzaldehyde. Reagents and conditions: i, $SnBr_4$, −78 °C, 5 min, PhCHO, −78 °C, 1 h (64%, **116** : **120** ≥ 98 : 2); ii, TBSCl, imid., DCM, r.t., 30 min (67%); iii, 4-$O_2NC_6H_4CO_2H$, PPh_3, DIAD, 0 °C, 10 min, r.t., 30 min (63%); iv, NaOH, MeOH, r.t., 2 h; v, TBAF, THF, r.t., 15 h (89%).

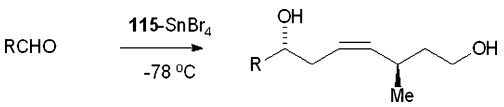
As the compounds in this series were racemic, ozonolysis or *O*-acetylmandelates couldn't be used to establish their relative configuration. The 1,5-*anti*-diol **116** was therefore taken through to lactone **125** to see whether transannular nOe measurements would confirm the assigned stereochemistry, see Scheme 12. The diol was protected as its bis-*tert*-butyldimethylsilyl ether **121** which was selectively monodesilylated using HF-pyridine to alcohol **122**. Oxidation *via* the corresponding aldehyde gave the carboxylic acid **123** and, after desilylation to give the hydroxyacid **124**, lactonisation[17] gave the lactone **125**. This confirmed the (*Z*)-geometry assigned to the double-bond, but nOe studies did not establish the relative configuration of the stereogenic centres. The 1,5-*anti*-configuration was therefore assigned to products in this series on the basis of the supposed mechanism and by analogy to the other series, *vide infra*.



Scheme 12 Synthesis of lactone **125**. Reagents and conditions: i, TBSCl, imid., DMAP, r.t., 18 h (82%); ii, HF-py., THF, 18 h (72%); iii, Dess—Martin periodinane, $NaHCO_3$, DCM, r.t., 1 h; iv, $NaClO_2$, NaH_2PO_4, 2-methylbut-2-ene, ^{t}BuOH, H_2O, r.t., 2 h (76% from **122**); v, HCl, MeOH, r.t., 2 h (80%); vi, 2,4,6-$Cl_3C_6H_2COCl$, Et_3N, THF, r.t., 2 h, then DMAP, toluene, reflux, 4.5 h (60%).

The 6-hydroxy-4-methylhexenylstannane **115** was then reacted with a range of aldehydes using tin(IV) bromide to effect transmetallation, and the results obtained are shown in Table 4. In all cases high levels of stereoselectivity were observed by NMR, and in some cases, by glc. The 1,5-*anti*-configuration of the products was assigned by analogy with earlier work and the (*Z*)-geometry of the double-bond was confirmed by the vinylic ^{1}H coupling constants which were in the range of 10–11 Hz.

Table 4 1,5-Stereocontrol in tin(IV) bromide mediated reactions between aldehydes and allylstannane **115**

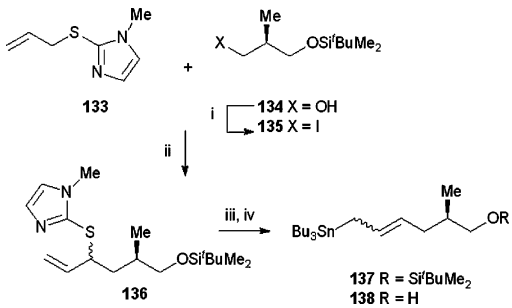


R	1,5-*anti*-product[a]	Yield (%)	1,5-*anti* : 1,5-*syn*
Ph	**116**	64	99 : 1
4-$MeOC_6H_4$	**126**	61	99 : 1[b]
4-ClC_6H_4	**127**	74	98 : 2[b]
3-ClC_6H_4	**128**	64	99 : 1[b]
4-$O_2NC_6H_4$	**129**	62	99 : 1[b]
Me_2CH	**130**	63	91 : 9[c]
^{n}Pr	**131**	67	96 : 4[c]
MeCH═CH	**132**	76	97 : 3[c]

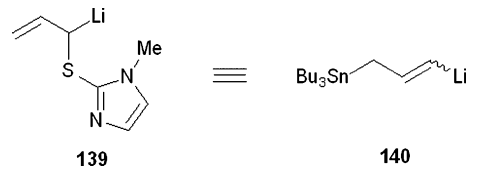
[a] In all cases the vicinal vinylic coupling constant was *ca.* 10 Hz. [b] Ratio by ^{1}H NMR. [c] Ratio by glc.

1,6-Stereocontrol using 5-methyl-6-hydroxyhex-2-enylstannnane IV (R = H)

A synthesis of the 6-hydroxy-5-methylhex-2-enylstannane **138** is outlined in Scheme 13. Following lithiation, the allyl sulfide **133**[18] was alkylated using iodide **135**, which is available from alcohol **134**, to give a mixture of the epimeric alkylated sulfides **136**. Reaction of this mixture with tributyltin hydride under free-radical conditions gave the 6-silyloxyhexenylstannane **137** which was deprotected to give the 6-hydroxy-5-methylhexenylstannane **138**, (*E*) : (*Z*) = 2 : 1, see Scheme 13. In this two step synthesis of alk-2-enylstannanes from alkyl halides, the lithiated allylsulfide **139** is being used as the synthetic equivalent of 3-(tributylstannyl)propenyllithium **140**,[19] see Fig. 4.



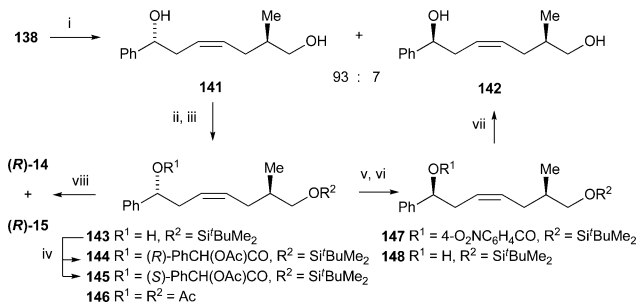
Scheme 13 Synthesis of the 6-hydroxy-5-methylhexenylstannane **138**. Reagents and conditions: i, (a) MsCl, Et_3N, DCM, −20 °C to r.t., 1 h (*ca.* 100%) (b) NaI, acetone, heat, 18 h (70%); ii, **133**, *n*BuLi, THF, HMDA, −78 °C, 30 min, **135**, −78 °C, 2.5 h (42%); iii, Bu_3SnH, AIBN, benzene, heat, 18 h [79%, (*E*) : (*Z*) = 2 : 1]; iv, TBAF, THF, r.t., 18 h (79%).



139 **140**

Fig. 4 The synthetic equivalence of the lithiated allylsulfide **139** and 3-(tributylstannylpropenyl)lithium **140**.

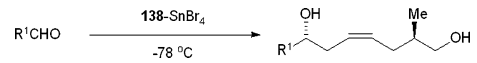
The tin(IV) bromide mediated reaction of the 5-methylhexenylstannane **138** with benzaldehyde was stereoselective in favour of the (*Z*)-1,6-*anti*-heptenediol **141**, 1,6-*anti* : 1,6-*syn* = 93 : 7, see Scheme 14. With tin(IV) chloride, the stereoselectivity dropped to 84 : 16 and the yield to 62%. To establish the stereoselectivity of this reaction, the (*Z*)-1,5-*anti*-product **141** was converted into its 1,6-*syn*-epimer **142** by selective protection as its monosilyl ether **143**, inversion of configuration at C(1) using a Mitsunobu reaction, hydrolysis of the ester **147** and desilylation of the resulting (*Z*)-1,6-*syn*-silyloxyalcohol **148**. The 1,6-*anti*- and 1,6-*syn*-diols **141** and **142** were distinguishable by ^{1}H NMR and their ratio was measured by integration of 1-H, which was observed at δ4.65 for the *anti*-diol **141** and at δ4.71 for its *syn*-epimer **142**. The configuration of the major product **141** at C(1) was initially assigned on the basis of the ^{1}H NMR chemical shifts of the (*R*)- and (*S*)-*O*-acetylmandelates **144** and **145** prepared from the monosilylether **143**, and was confirmed by ozonolysis of the diacetate **146** which gave the (*R*)-3-acetoxy-3-phenylpropanol (*R*)-**14** together with the product (*R*)-**15** of acetate migration.[1a]



Scheme 14 1,6-Stereocontrol in the reaction of 6-hydroxyhexenylstannane **138** and benzaldehyde. Reagents and conditions: i, $SnBr_4$, DCM, –78 °C, 10 min, PhCHO, –78 °C, 1 h (84%; **141** : **142** = 93 : 7); ii, TBSCl, Et_3N, DMAP, DCM, r.t., 3 h (92%); iii, Ac_2O, Et_3N, DMAP, DCM, r.t., 18 h (90%); iv, (*R*)- or (*S*)-*O*-acetylmandelic acid, DCC, DMAP, DCM, r.t. 18 h (**144**, 90%; **145**, 80%); v, 4-$O_2NC_6H_4CO_2H$, Ph_3P, DEAD, toluene, –35 °C, 90 min (69%); vi, NaOH, MeOH, r.t., 3 h (73%); vii, TBAF, THF, r.t., 18 h (88%); viii, O_3, DCM, –78 °C, 40 min, DMS, then DCM, $NaBH_4$, MeOH, r.t., 2 h [(*R*)-**14**, 34%; (*R*)-**15**, 16%].

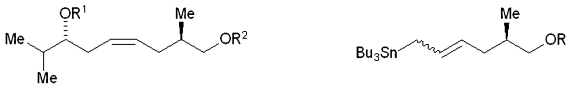
Tin(IV) bromide mediated reactions of the allylstannane **138** with several aldehydes were investigated, and the results are summarised in Table 5. In all cases, useful stereoselectivities in favour of the (*Z*)-1,6-*anti*-isomers were observed as estimated by ^{1}H NMR. The 1,6-*anti*-configuration of the major product from the reaction of the alkenylstannane **138** with 2-methylpropanal was established by comparison of the ^{1}H NMR spectra of the (*R*)- and (*S*)-*O*-acetylmandelates **154** and **155** prepared from the monosilyl ether **153**. The structures of the other products were assigned by analogy.

Table 5 1,6-Stereocontrol in tin(IV) bromide mediated reactions between aldehydes and allylstannane **138**



R^1	1,6-*anti*-product[a]	Yield (%)	1,6-*anti* : 1,6-*syn*
Ph	**141**	84	93 : 7
4-$MeOC_6H_4$	**149**	58	91 : 9[b]
4-$O_2NC_6H_4$	**150**	76	91 : 9[b]
Et	**151**	56	93 : 7[c]
Me_2CH	**152**	80	91 : 9[d]

[a] In all cases the vicinal vinylic coupling was 10 Hz. [b] Ratio by ^{1}H NMR. [c] Ratio by pulse delayed ^{13}C NMR. [d] Ratio by pulse delayed ^{13}C NMR; stereochemistry by comparison of the ^{1}H NMR spectra of the (*R*)- and (*S*)-*O*-acetylmandelates **153** and **154**.



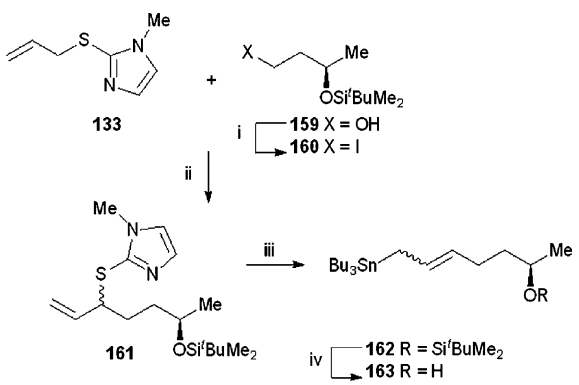
153 R^1 = H, R^2 = Si^{t}BuMe$_2$
154 R^1 = (*R*)-PhCH(OAc)CO, R^2 = Si^{t}BuMe$_2$
155 R^1 = (*S*)-PhCH(OAc)CO, R^2 = Si^{t}BuMe$_2$

156 R = Me
157 R = CH_2OMe
158 R = Bn

The 6-hydroxyhexenylstannane **138** was also converted into its methyl, MOM and benzyl ethers **156–158**. However, tin(IV) bromide mediated reactions of these with benzaldehyde were less stereoselective than those observed for the 6-hydroxyhexenylstannnane **138**, the 1,6-*anti* : 1,6-*syn* ratios typically being of the order of 60 : 40, although (*Z*)-alkenols remained the dominant products.

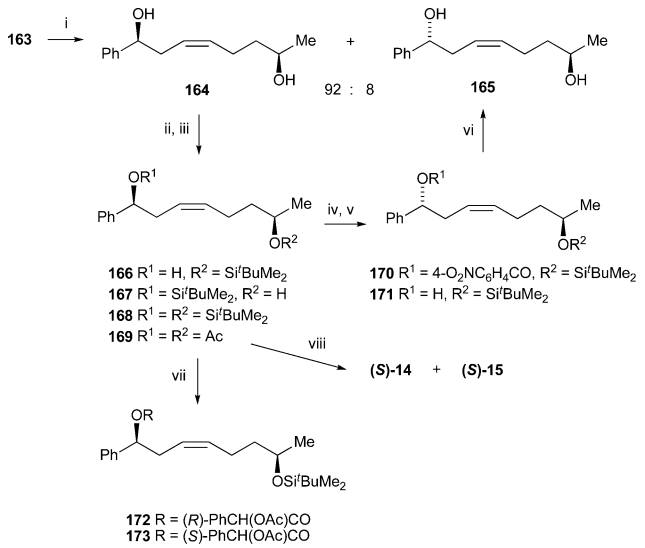
1,7-Stereocontrol using 6-hydroxyhept-2-enylstannnane V (R = H)

1,7-Remote stereocontrol is rare in open-chain systems and so the chemistry of 6-hydroxyhept-2-enylstannane **163**, in which there is potential for 1,7-stereocontrol determined by the stereogenic centre at C(6), was investigated. This stannane was prepared by alkylation of the allylsulfide **133** using the alkyl iodide **160** prepared from the alcohol **159**,[20] see Scheme 15. Reaction of the alkylated sulfide **161** with tributyltin hydride under free-radical conditions gave the 6-hydroxyheptenylstannane **163** after desilylation of the silyl ether **162**.



Scheme 15 Synthesis of the 6-hydroxyhept-2-enylstannane **163**. Reagents and conditions: i, Ph_3P, imid., ether, MeCN, I_2, 0 °C, r.t., 2.5 h (75%); ii, *n*BuLi, hexane, **133**, –78 °C, 20 min, **160**, –78 °C, 2.5 h (83%, a 1 : 1 mixture of epimers); iii, Bu_3SnH, AIBN (trace), benzene, heat, 1.5 h (92%); iv, TBAF, THF, r.t., 50 h [80%, (*E*) : (*Z*) = 2 : 1].

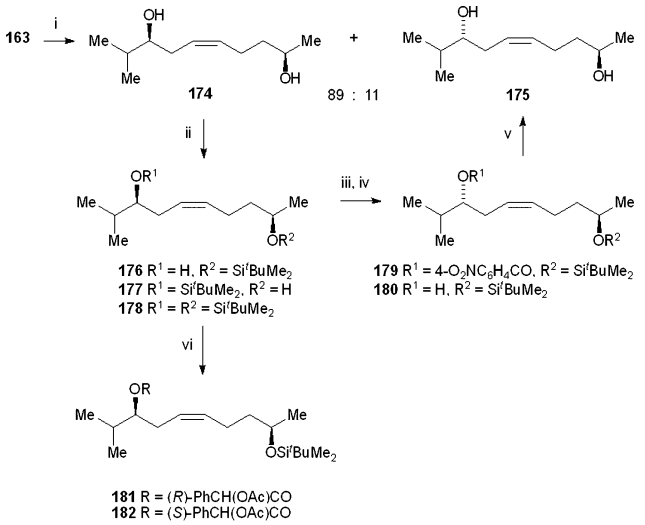
The tin(IV) bromide mediated reaction of the heptenylstannane **163** with benzaldehyde gave the (*Z*)-1,7-*syn* and (*Z*)-1,7-*anti*-products **164** and **165** with useful stereoselectivity, **164** : **165** = 92 : 8, together with a third product accounting for *ca.* 2% of the product mixture, which was not identified. To confirm that the minor product from the reaction of the stannane **163** with benzaldehyde was the (*Z*)-1,7-*anti*-isomer **165**, an authentic sample was prepared, see Scheme 16. Silylation of the 1,7-*syn*-diol **164** gave the regioisomeric monosilyl ethers **166** (63%) and **167** (5%), together with the bis-silyl ether **168** (15%). Inversion of the monosilyl ether **166** at C(1) using a Mitsunobu reaction provided the 1,7-*anti*-silyloxy ester **170** which was converted to the 1,7-*anti*-diol **165** by saponification and deprotection of the resulting monosilyl ether **171**. Diols **164** and **165** were distinguishable by ^{1}H and ^{13}C NMR *e.g.* 1-H was observed at δ4.72 and at δ4.63 in the ^{1}H NMR spectra of the 1,7-*syn* and 1,7-*anti*-isomers **164** and **165**, respectively.



Scheme 16 1,7-Stereocontrol in the reaction of 6-hydroxyhept-2-enylstannane **163** and benzaldehyde. Reagents and conditions: i, **163**, $SnBr_4$, DCM, −78 °C, 10 min, add PhCHO, −78 °C, 1 h (72%, **164** : **165** = 92 : 8); ii, TBSCl, imid., DMF, r.t., 15 h (**166**, 63%; **167**, 5%; **168**, 15%); iii, Ac_2O, Et_3N, DMAP, DCM, r.t., 15 h (96%); iv, 4-$O_2NC_6H_4CO_2H$, Ph_3P, DEAD, toluene, −35 °C, r.t., 2 h (74%); v, NaOH, MeOH, r.t., 2 h (93%); vi, TBAF, THF, r.t., 72 h (96%); vii, (*R*)- or (*S*)-*O*-acetylmandelic acid, DCC, DMAP, DCM, r.t. 18 h (**172**, 78%; **173**, 83%); viii, O_3, DCM, −78 °C, 15 min, DMS, then DCM, $NaBH_4$, MeOH, r.t., 15 min [(*S*)-**14**, 27%; (***S***)-**15**, 13%].

The 1,7-*syn*-configuration was assigned to the major product **164** by comparison of the ^{1}H NMR spectra of the (*R*)- and (*S*)-*O*-acetylmandelates **172** and **173** prepared from the monosilyl ether **166**, and was confirmed by ozonolysis of the bis-acetate **169** which gave (*S*)-3-acetoxy-3-phenylpropan-1-ol (*S*)-**14** and the (*S*)-3-acetoxy-1-phenylpropan-1-ol (*S*)-**15**, formed by 1,3-acetate migration,[1a] see Scheme 16. The (*Z*)-configuration of the double-bond was consistent with the 10.5 Hz vinylic ^{1}H coupling observed for the 1,7-*syn*-diol **164**.

The tin(IV) bromide promoted reaction of the 6-hydroxyhex-2-enylstannane **163** with 2-methylpropanal was also stereoselective in favour of the (*Z*)-1,7-*syn*-product **174**, (*Z*)-1,7-*syn*-diol **174** : (*Z*)-1,7-*anti*-diol **175** = 89 : 11, see Scheme 17. A small



Scheme 17 1,7-Stereocontrol in the reaction of 6-hydroxyhept-2-enylstannane **163** and 2-methylpropanal. Reagents and conditions: i, **163**, $SnBr_4$, DCM, −78 °C, 10 min, add ^{i}PrCHO, −78 °C, 1 h (63%, **174** : **175** = 89 : 11); ii, TBSCl, imid., DMF, r.t., 15 h (**176**, 65%; **177**, 1%; **178**, 9%); iii, 4-$O_2NC_6H_4CO_2H$, Ph_3P, DEAD, toluene, −35 °C, r.t., 5 h (61%); iv, NaOH, MeOH, r.t., 3 h; v, TBAF, THF, r.t., 50 h (66% from **179**); vi, (*R*)- or (*S*)-*O*-acetylmandelic acid, DCC, DMAP, DCM, r.t. 18 h (**181**, 95%; **182**, 74%).

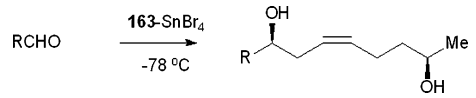
amount, *ca.* 2%, of a third product was also isolated but was not identified.

To check the structure of the minor product **175**, a sample was prepared by silylation of the major 1,7-*syn*-diol **174**. This gave a mixture of the regioisomeric monosilyl ethers **176** (65%) and **177** (1%), together with the bis-silyl ether **178** (9%). A Mitsunobu reaction of the major monosilyl ether **176** using 4-nitrobenzoic acid gave the inverted ester **179**, which was converted into the 1,7-*anti*-diol **175** by saponification and desilylation of the monosilyl ether **180**. The 1,7-*syn*- and 1,7-*anti*-diols **174** and **175** were difficult to distinguish by ^{1}H NMR but were distinguishable by ^{13}C NMR. Pulse delayed ^{13}C NMR was used to measure their ratio in the product mixture from the allylstannane reaction. The configuration of the hydroxyl bearing stereogenic carbon in the monosilyl ether **176** was established by comparison of the ^{1}H NMR spectra of the (*R*)- and (*S*)-*O*-acetylmandelates **181** and **182**.

Tin(IV) bromide promoted reactions of the 6-hydroxyhept-2-enylstannane **163** with several aromatic and aliphatic aldehydes were investigated, and the results obtained are shown in Table 6. In all cases useful levels of stereoselectivity in favour of the (*Z*)-1,7-*syn*-products were observed. The structures of the major products were consistent with spectroscopic data. The 1,7-*syn*-diastereoselectivity and structures of the minor products were assigned by analogy with the reactions of stannane **163** with benzaldehyde and 2-methylpropanal. Product ratios were measured by ^{1}H NMR for the products from aromatic aldehydes and by ^{13}C pulse delayed NMR for the products from aliphatic aldehydes.

The tin(IV) chloride mediated reaction of the 6-hydroxyheptenylstannnane **163** with benzaldehyde gave the *syn*- and (*Z*)-1,7-*anti*-products **164** and **165**, but the stereoselectivity was only 75 : 25 in favour of the 1,7-*syn*-diastereoisomer **164**. The hydroxyheptenylstannane **163** was also converted into the

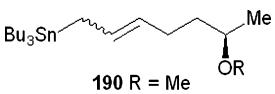
Table 6 1,7-Stereocontrol in tin(IV) bromide mediated reactions between aldehydes and allylstannane **163**



R	1,7-*syn*-product[a]	Yield (%)	1,7-*syn* : 1,7-*anti*
Ph	**164**	72	92 : 8
4-$MeOC_6H_4$	**183**	47	89 : 11[b]
4-ClC_6H_4	**184**	71	92 : 8[b]
2-naphth.	**185**	65	93 : 7[b]
Me_2CH	**174**	63	89 : 11
Me	**186**	36	90 : 10[c]
Et	**187**	61	91 : 9[c]
Me_2CHCH_2	**188**	58	85 : 15[c]
Me_3C	**189**	38	95 : 5[c]

[a] Minor product assumed to be the (*Z*)-1,7–isomer by analogy with the reactions of benzaldehyde and 2-methylpropanal with stannane **163**; a third very minor product, *ca.* 1%, also detected but not identified. [b] Ratio by ^{1}H NMR. [c] Ratio by pulse-delayed ^{13}C NMR.

6-methoxy-, 6-(methoxymethoxy)- and 6-benzyloxystannanes **190–192**, but preliminary studies of tin(IV) halide promoted reactions of these with aldehydes gave mixtures of products, and so were not studied further.

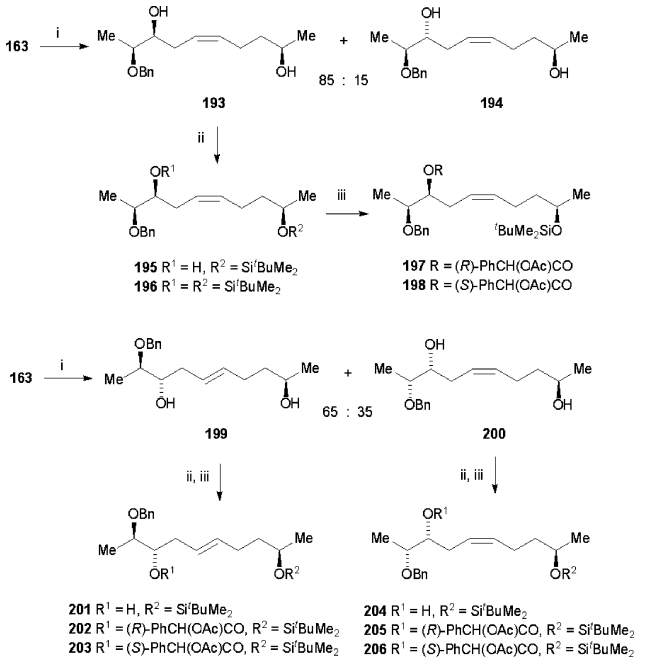


190 R = Me
191 R = MOM
192 R = Bn

Tin(IV) bromide promoted reactions of the 6-hydroxyheptenylstannane **163** with the chiral aldehydes (*S*)- and (*R*)-2-benzyloxypropanal were also investigated, see Scheme 18. With the (*S*)-enantiomer, the (*Z*)-1,7-*syn*- and (*Z*)-1,7-*anti*-products **193** and **194** were obtained, the 1,7-*syn* : 1,7-*anti* ratio of 85 : 15 being measured by ^{13}C pulse delayed NMR. The geometry of the double-bond of the major product **193** followed from its vicinal vinylic ^{1}H NMR coupling constant (10.5 Hz) and its 1,7-*syn*-configuration was established by comparison of the ^{1}H NMR spectra of the (*R*)- and (*S*)-*O*-acetylmandelates **197** and **198** prepared from the monosilyl ether **195**. The structure of the minor product was assigned by analogy with the identification of the (*Z*)-1,7-*anti*-isomers **165/175** as the minor products from the reaction of stannane **163** with benzaldehyde and 2-methylpropanal.

The tin(IV) bromide promoted reaction of the (*R*)-2-benzyloxypropanal and the (*R*)-6-hydroxyheptenylstannane **163** was less stereoselective and gave two separable products, ratio 65 : 35. Unexpectedly, the major product was found by spin decoupling to have a vinylic coupling constant of 15 Hz, indicative of an (*E*)-alkene. To establish their configuration at the newly introduced hydroxyl bearing carbon, following selective monosilylation, both products were converted into (*R*)- and (*S*)-*O*-acetylmandelates, see Scheme 18. By comparison of the ^{1}H NMR spectra of the *O*-acetylmandelates **202/203** and **205/206** derived from each silyl ether, and taking into account the double-bond geometries as indicated by ^{1}H NMR, the major product was identified as the (*E*)-1,7-*anti*-diol **199** and the minor as the (*Z*)-1,7-*anti*-diol **200**.

The reaction of the (*R*)-6-hydroxyheptenylstannane **163** with (*R*)-2-benzyloxpropanal was the only example found during the



Scheme 18 Reactions of (*S*)- and (*R*)-2-benzyloxypropanal with the 6-hydroxyhept-2-enylstannane **163**. Reagents and conditions: i, $SnBr_4$, –78 °C, 10 min, (*S*)- or (*R*)-MeCH(OBn)CHO, –78 °C, 1 h (**193**, **194**, 56%; **199**, **200**, 67%); ii, TBSCl, imid., DMF. r.t., 15 h (**195**, 61%; **196**, 5%; **201**, 55%; **204**, 33%); iii, (*R*)- or (*S*)-*O*-acetylmandelic acid, DCC, DMAP, DCM, r.t. 18 h (**197**, 78%; **198**, 75%; **202**, 78%; **203**, 75%; **205**, 89%; **206**, 88%).

course of this work where the major product from a tin(IV) halide promoted reaction of a heterofunctionalised alk-2-enylstannane had an (*E*)-double-bond. It is likely that the formation of the (*E*)-isomer **199** is indicative of an open-chain transition structure in the reaction of the intermediate allyltin tribromide with the aldehyde, but why this particular combination of reagents proceeds *via* an open-chain process rather than *via* the more usually observed 6-membered chair-like transition structure is not clear.

Apart from this exception, the stereoselectivities observed for all the tin(IV) bromide promoted reactions of the 6-hydroxyalk-2-enylstannanes **115**, **138** and **163** with aldehydes are consistent with kinetically controlled, stereoselective transmetallations generating allyltin tribromides which react with aldehydes *via* six-membered chair-like transition structures, see Fig. 5. It is proposed that the stereogenic centre in the alk-2-enylstannane controls the facial selectivity of the transmetallation to give the allyltin tribromides **207**, **210** and **213**, in which the methyl and ethenyl substituents are pseudoequatorial about the six-membered oxastannane ring formed by co-ordination of the hydroxyl group with the electron deficient tin. These allyltin tribromides can then react with aldehydes *via* the six-membered chair-like transition structures **208**, **211** and **214** to give the (*Z*)-1,5-*anti*-, the (*Z*)-1,6-*anti*- and the (*Z*)-1,7-*syn*-products **209**, **212** and **215**, respectively. The formation of the (*Z*)-double-bonds in these products is consistent with the known preference of a group next to tin to adopt the axial position in analogous chair-like transition structures. This preference together with the preference of the R group of the aldehyde to adopt the equatorial position, explains how the allyltin

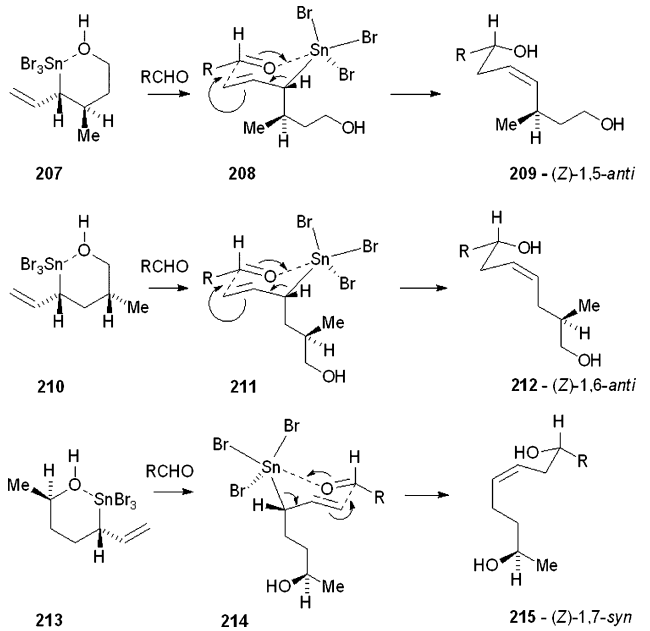


Fig. 5 Participation of allyltin tribromides which account for the stereoselectivity observed for the tin(IV) bromide promoted reactions of allylstannanes **116**, **138** and **163** with aldehydes.

tribromides **207**, **210** and **213**, deliver the remote stereocontrol which is observed, *cf*. the generalised structures **209**, **212** and **215** in Fig. 5 with the structures of the products obtained from alk-2-enylstannanes **115**, **138** and **163** in Tables 4, 5 and 6.

Summary and conclusions

This work has shown that allylstannanes with an alkoxy or hydroxy substituent at the 4-, 5- or 6-position react with tin(IV) halides at –78 °C to generate intermediates, believed to be allyltin trihalides, which react with aldehydes with useful levels of 1,5-, 1,6- and 1,7-stereocontrol. Fig. 6 shows an overview of the results obtained. Interestingly, stannanes **1**, **73/74** and **163** with a stereogenic carbon bearing a secondary alkoxy- or hydroxy-substituent at either the 4-, 5- or 6-position react with overall (*Z*)-1,5-, (*Z*)-1,6- and (*Z*)-1,7-*syn*-stereocontrol. In contrast, stannanes **6**, **34/35**, **115** and **138** with a terminal alkoxy- or hydroxy-substituent and a stereogenic carbon bearing a methyl substituent at either the 4- or 5-position, react with overall (*Z*)-1,5- or (*Z*)-1,6-*anti*-stereocontrol.

Details of mechanistic studies including studies into the trapping of the allyltin trihalides **28** and **216** and evidence for kinetic control of the transmetallation step will be reported in full elsewhere. However, the overall remote stereoselectivity which is reported here is believed to be due to two factors:

(a) the kinetically controlled, diastereofacially selective transmetallation of substituted allylstannanes by the tin(IV) halide to form allyltin trihalides with high levels of stereoselectivity,[21] and

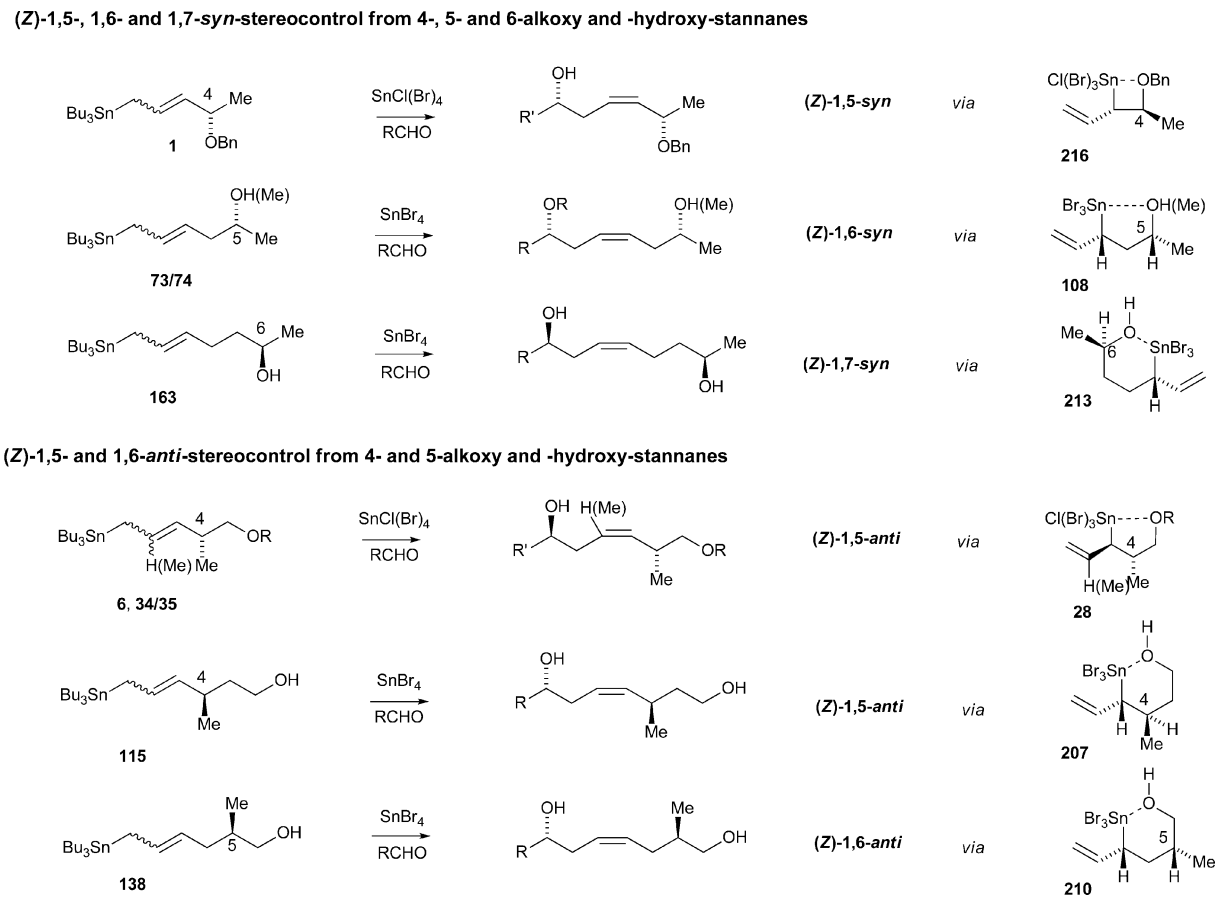


Fig. 6 Overview of remote stereocontrol using alkoxy and hydroxy-alk-2-enylstannanes.

(b) the subsequent reaction of the allyltin trihalides with aldehydes *via* six-membered chair-like transition structures in which the group next to tin adopts an axial position.[22]

The allylstannanes used in this work were mixtures of (*E*)- and (*Z*)-isomers, typically (*E*) : (*Z*) = 70 : 30. No attempts were made to study reactions of the (*E*)- and (*Z*)-isomers separately although studies of the analogous chemistry of alk-2-enylgermanium compounds indicated that (*Z*)-isomers were transmetallated with better stereoselectivity.[23] To explain the high levels of stereocontrol in the transmetallation step, even for 5- and 6-substituted alk-2-enylstannanes, it is suggested that the tin halide initially co-ordinates to the alkoxy or hydroxy group and is then delivered to the double-bond of the allylstannane *via* an intramolecular process. For example, formation of the allyltin trichloride **28** from both the (*E*)- and *Z*)-isomers of the (*R*)-4-methylpent-2-enylstannane **6** *via* intramolecular delivery of the trichlorotin moiety to the double-bond places the methyl substituent in the less hindered "outside" position, see transition structures **217** and **219** in Fig. 7. Formation of the isomeric allyltin trichloride **221** in which the vinyl and methyl groups are *cis*-disposed with respect to the 5-membered oxastannane ring would require the methyl group to be in the more hindered "inside" position, see transition structures **218** and **220**. Note that the stereochemistry of the tin(IV) halide mediated transmetallation of allylstannanes by tin(IV) halides has not been defined. An antarafacial process is depicted in Fig. 7 but an alternative 6-membered, cyclic, suprafacial process could be involved. However, the explanation given for the introduction of the stereogenic centre bearing the tin into the intermediate allyltin trihalides would still be valid.[21]

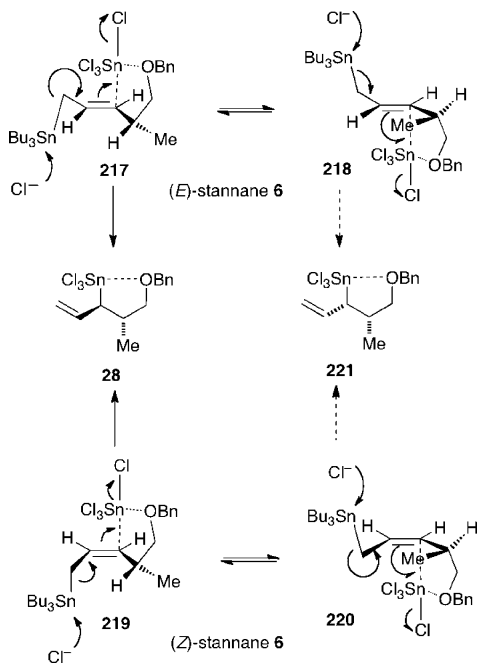
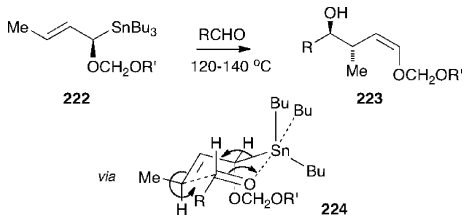


Fig. 7 Transmetallation of the (*E*)- and (*Z*)-isomers of the alk-2-enylstannane **6**.

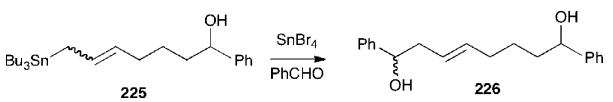
In the second step, the reaction of the allyltin trihalide with the aldehyde, the high fidelity for formation of (*Z*)-double-bonds in the products is consistent with the participation of 6-membered chair-like transition structures, in which the tin is trigonal bipyramidal, *i.e.* transition structures **29**, **109**, **208**, **211** and **214**.

1-Substituted alk-2-enylstannanes are known to react with aldehydes on heating to give (*Z*)-alkenes; for example the highly stereoselective synthesis of the (*Z*)-1,2-*anti*-alkenes **223** from the non-catalysed reactions of 1-alkoxybut-2-enylstannanes **222** with aldehydes. The six-membered chair-like transition state **224** in which the group α to the tin is in the axial position, has been suggested to explain the stereoselectivity observed in these reactions.[22]



The transition structures **29**, **109**, **208**, **211** and **214** which involve a 1-substituted allyltin trichloride reacting with an aldehyde with formation of an (*Z*)-alkene, are analogous to the transition structure **224** proposed for the thermal process. In particular, is suggested that the alkoxy or hydroxy group, which initially directed the transmetallation, is no longer bound to the tin in these transition structures. The high preference for (*Z*)-alkene formation, especially for reactions in which the co-ordinating group is at the 6-position in the allylstannane, is difficult to reconcile with transition structures in which the tin is hexacoordinated, *i.e.* octahedral.

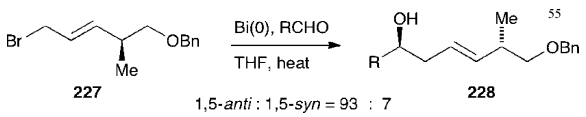
This remote stereocontrol using tin(IV) halide mediated reactions of alkoxy and hydroxy-functionalised alk-2-enylstannanes would appear to be generally useful and reliable with better stereoselectivity obtained using tin(IV) bromide and 6-hydroxyalk-2-enylstannanes for 1,6- and 1,7-stereocontrol. Preliminary studies to extend this work to include 1,8-stereocontrol using 7-hydroxy-7-phenylhept-2-enylstannane **225** were unsuccessful, in that a mixture of the (*E*)-1,8-*syn*-and 1,8-*anti*-diphenyloct-3-ene-1,8-diols **225** was obtained (81%, 2 : 1). However, 1,8- and 1,9-stereocontrol has been achieved by combining 1,5-stereocontrol as discussed here, with subsequent stereoselective 2,3- and 3,3-sigmatropic rearrangements.[24,25]



This chemistry has the limitation that it involves the use of organotin reagents, indeed one equivalent of tributyltin chloride or bromide is produced as the side-product in the transmetallation step. Analogous allylsilanes undergo transmetallation with tin(IV) halides but, under the longer reaction times required, the intermediate allyltin trihalides begin to equilibrate with their epimers and only modest stereoselectivities are observed.[26] However, allylgermanes undergo transmetallation at −78 °C relatively quickly, and 1,5- and 1,6-remote stereocontrol has been shown for reactions with aldehydes of 5- and 6-alkoxy and -hydroxy-alk-2-enylgermanes. Indeed when using tin(IV) bromide and (*Z*)-alk-2-enylgermanes higher stereoselectivities can be obtained than those found using the corresponding allylstannanes.[23]

Bismuth tri-iodide also effects transmetallation of the allylstannane **6** to generate an allylbismuth intermediate which reacts with

aldehydes with useful 1,5-stereocontrol, albeit in favour of (*E*)-alk-3-enols.[27] Similar stereoselectivity has also been observed for the bismuth(0) promoted reactions of 5-alkoxy-4-methylpent-2-enyl bromides with aldehydes, a tin-free process, for example the formation of the (*E*)-alkenols **228** from the bromide **227** and a reduced bismuth species.[28]



227 **228**

1,5-*anti* : 1,5-*syn* = 93 : 7

Finally, 1,5-stereocontrol has also been observed for tin(IV) halide promoted reactions of amino- and phenylthio-substituted alkenylstannanes with aldehydes, and for reactions of 4- and 5-alkoxyalk-2-enylstannanes with reactive imines.[29–31] Details of this work and of the application of remote stereocontrol using tin(IV) halide mediated reactions of allylstannanes to complete syntheses of the natural products, patulolide C,[24] epothilones[32] and pamamycin 607,[33] will be reported in full elsewhere.

Experimental

General experimental procedures

NMR spectra were recorded on Varian Unity 500, Bruker AC-300 or Varian XL spectrometers and IR spectra on a Perkin–Elmer 1710FT spectrometer. For minor diastereoisomers, >10%, present in mixtures, just the distinctive peaks are reported. Low resolution chemical ionisation (CI) and electron impact (EI) mass spectra were recorded on a Kratos MS25 mass spectrometer coupled to a DS 55 data system or on a VG Trio 2000 mass spectrometer. Fast atom bombardment (FAB) mass spectra and all high resolution mass spectra were recorded on a Kratos Concept 1S mass spectrometer coupled to a Mach 3 data system. Compounds containing tin or chlorine showed characteristic clusters of isotope peaks in their mass spectra.

Optical rotations were recorded on an Optical Activity AA-100 polarimeter at 589 nm using chloroform as the solvent at ambient temperature. Analytic high performance liquid chromatography was carried out with a Waters Z module, 10 cm × 8 mm cartridge, C18 5 m stationary phase and detection by ultraviolet absorption using a Perkin–Elmer IC-480 detector at 255 nm. Semi-preparative high performance liquid chromatography was carried out using a Gilson 303 pump (with manometric module), Dynamax 83-211-C column 25 cm × 10 mm, 8 m silica, detection with a Gilson 131 refractive index detector and Gilson 115 UV detector at 254 nm. Chromatography refers to flash chromatography and was carried out using Merck silica 60H (40–60 m, 230–300 mesh) or May and Baker Sorbsil C60 silica gel (40–60 m) as the stationary phase.

Petrol refers to light petroleum which distils between 40 °C and 60 °C. Tin(IV) chloride was dried with phosphorus pentoxide and distilled. Ether refers to diethyl ether. Brine refers to saturated aqueous sodium chloride. All solvents were dried and distilled before use.

Alcohol **3** was prepared as described in the literature.[5] Its e.e. was estimated by ozonolysis with a reductive work-up to give (*R*)-3-benzyloxy-2-methylpropanol shown to have an e.e. of >85% by Mosher's derivatisation.

General procedure for the reaction of an alkoxyalk-2-enylstannane with an aldehyde in the presence of a Lewis acid

The tin(IV) halide (1.044 M in DCM, 958 µl, 1.00 mmol) was added to the stannane (1.0 mmol) in DCM (10 ml) at −78 °C. After 10 min, the aldehyde (3.48 M in DCM, 287 µl, 1.00 mmol) was added and the mixture was maintained at −78 °C for 1 h. Saturated aqueous sodium hydrogen carbonate (5 ml) was added and the mixture allowed to warm to room temperature. Ether (50 ml) and water (50 ml) were added and the organic phase was washed with aqueous ammonia (10%, 50 ml) and brine (50 ml), then dried ($MgSO_4$). Concentration under reduced pressure and chromatography of the residue gave the products as colourless oils.

General procedure for the preparation of Mosher's derivatives[34]

The alcohol (0.10 mmol) in carbon tetrachloride (300 µl) was added to the 2-methoxy-2-phenyl-3,3,3-trifluoropropanoyl chloride (0.20 mmol) in pyridine (300 µl) at room temperature and the mixture stirred until no starting material remained, typically 1–1.5 h (TLC). 3-Dimethylaminopropylamine (400 µl) was added and the clear solution was stirred for 10 min. Ether (25 ml) and water (25 ml) were added and the organic phase was washed with dilute aqueous hydrogen chloride (1 M, 20 ml), saturated aqueous sodium carbonate (20 ml) and brine (20 ml), then dried ($MgSO_4$). Concentration under reduced pressure gave the Mosher's ester as a colourless oil.

General procedure for the preparation of *O*-acetylmandelates

2-Acetoxy-2-phenylacetic acid (0.30 mmol), DCC (0.30 mmol) and 4-*N*,*N*-dimethylaminopyridine (0.005 mmol) were added to the alcohol (0.10 mmol) in DCM (2 ml) and the mixture stirred at room temperature for 15 h. DCM (15 ml) and water (15 ml) were added and the organic phase washed with dilute aqueous hydrogen chloride (3.5 M, 10 ml), saturated aqueous sodium hydrogen carbonate (10 ml) and brine (10 ml), then dried ($MgSO_4$). Concentration under reduced pressure left a solid which was absorbed onto silica. Chromatography gave the *O*-acetylmandelate as a colourless oil.

O-[(*R*)-5-Benzyloxy-4-methylpent-2-enyl]-*S*-methyl dithiocarbonate 4

Alcohol **3** [(*E*) : (*Z*) = 80 : 20; 3.39 g, 16.46 mmol) in benzene (16 ml) was added to sodium hydride (723 mg; 60% in mineral oil, 18.08 mmol) in benzene (16 ml) at 5 °C. After 1 h at room temperature, carbon disulfide (5.00 g, 65.76 mmol) was added at 5 °C and the mixture was stirred at room temperature for 3 h. Methyl iodide (9.34 g, 65.76 mmol) was added and the mixture stirred for 15 h then filtered through celite washing the filter-cake with DCM (120 ml). The organic extracts were washed with brine (80 ml), dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the residue using petrol : ether (15 : 1) as eluent gave the title compound **4** (3.72 g, 76%) as a yellow oil, a 4 : 1 mixture of (*E*)- and (*Z*)-isomers, $[\alpha]_D$ −1.9 (c = 0.49) (Found: M^+ + H, 297.0986. $C_{15}H_{21}O_2S_2$ requires M, 297.0983); ν_{max}/cm^{-1} 2856, 1453, 1217, 1060, 970 and 737; δ_H (300 MHz, C_6D_6) 0.90 (0.6 H, d, J 7, 4-CH_3), 0.98 (2.4 H, d, J 7, 4-CH_3), 2.21 (0.6 H, s, SCH_3), 2.22 (2.4 H, s, SCH_3), 2.39 (0.8 H, m, 4-H), 2.74 (0.2 H, m, 4-H),

3.07–3.21 (2 H, m, 5-H_2), 4.33 (0.4 H, s, $PhCH_2$), 4.34 (1.6 H, s, $PhCH_2$), 4.98 (1.6 H, d, *J* 5.5, 1-H_2), 5.18 and 5.26 (each 0.2 H, dd, *J* 14, 7, 1-H), 5.43 (0.2 H, t, *J* 11.5, 3-H), 5.52–5.69 (1.8 H, m, 2-H and 3-H) and 7.17–7.36 (5 H, m, ArH); δ_C (75 MHz, C_6D_6) 16.4, 17.3, 18.6, 33.1, 36.8, 69.8, 72.9, 74.3, 74.6, 122.5, 122.7, 127.7, 128.3, 139.0, 140.0 and 215.8; *m*/*z* (CI, NH_3) 314 (M^+ + 18, 33%), 297 (M^+ + 1, 82) and 189 (100).

S-[(3*RS*,4*S*)-5-Benzyloxy-4-methylpent-1-en-3-yl]-*S*-methyl dithiocarbonate 5

The xanthate **4** (3.72 g, 12.57 mmol) was heated under reflux in toluene (150 ml) for 15 h. Concentration under reduced pressure gave the title compound **5** (3.72 g, 100%) as a yellow oil, a 1 : 1 mixture of epimers, $[\alpha]_D$ +1.5 (*c* = 0.52) (Found: M^+, 296.0909. $C_{15}H_{20}O_2S_2$ requires *M*, 296.0905); ν_{max}/cm^{-1} 2856, 1647, 1454, 1101, 924, 870 and 737; δ_H (300 MHz, $CDCl_3$) 0.98 (3 H, d, *J* 7, 4-CH_3), 2.18 (1 H, m, 4-H), 2.42 (1.5 H, s, SCH_3), 2.43 (1.5 H, s, SCH_3), 3.29–3.46 (2 H, m, 5-H_2), 4.44–4.52 (3 H, m, $PhCH_2$ and 3-H), 5.11–5.33 (2 H, m, 1-H_2), 5.80 (1 H, m, 2-H), 7.27–7.37 (5 H, m, ArH); δ_C (75 MHz, $CDCl_3$) 13.2, 13.3, 14.3, 14.5, 37.6, 37.8, 51.2, 51.5, 72.7, 72.7, 73.2, 73.4, 117.3, 118.2, 127.7, 127.8, 128.5, 134.8, 136.3, 138.6, 188.8 and 188.9; *m*/*z* (CI, NH_3) 314 (M^+ + 18, 5%), 297 (M^+ + 1, 24) and 91 (100).

(*R*)-5-Benzyloxy-4-methylpent-2-enyl(tributyl)stannane 6

Tributyltin hydride (4.80 g, 16.49 mmol) and azobis-*iso*-butyronitrile (135 mg, 0.825 mmol) were added to a degassed solution of the dithiocarbonate **5** (3.72 g, 12.57 mmol) in benzene (125 ml) and the solution was heated under reflux for 2.5 h. After concentration under reduced pressure, chromatography of the residue using petrol : ether (50 : 1 + 1% triethylamine) as eluent gave the title compound **6** (5.18 g, 86%) as a colourless oil, a 4 : 1 mixture of (*E*)- and (*Z*)-isomers), $[\alpha]_D$ −6.3 (*c* = 0.79); (Found: $M^+ - C_4H_9$, 423.1723. $C_{21}H_{35}O^{120}Sn$ requires *M*, 423.1710; ν_{max}/cm^{-1} 2956, 2925, 1455, 1095, 962 and 734; δ_H (300 MHz, $CDCl_3$) 0.78–0.98 (15 H, m, 3 × $SnCH_2CH_2CH_2CH_3$), 1.03 (3 H, m, 4-CH_3), 1.22–1.75 (14 H, m, 3 × $SnCH_2CH_2CH_2CH_3$ and 1-H_2), 2.48 (0.8 H, m, 4-H), 2.78 (0.2 H, m, 4-H), 3.24 (1 H, dd, *J* 8, 6, 5-H), 3.46 (1 H, m, 5-H′), 4.46–4.57 (2 H, m, $PhCH_2$), 4.89 (0.2 H, dd, *J* 10.5, 9.5, 3-H), 5.16 (0.8 H, dd, *J* 15, 7, 3-H), 5.53–5.67 (1 H, m, 2-H) and 7.25–7.38 (5 H, m, ArH); δ_C (75 MHz, $CDCl_3$) (*E*)-isomer 9.3, 13.9, 14.5, 17.9, 27.5, 29.3, 37.2, 73.1, 76.2, 127.6, 127.7, 128.1, 128.5, 129.3 and 139.0; *m*/*z* (EI) 423 (M^+ − 57, 54%), 291 (33) and 91 (100).

(1*S*,5*R*,3*Z*)-6-Benzyloxy-5-methyl-1-phenylhex-3-en-1-ol 7

Following the general procedure, stannane **6** (500 mg, 1.044 mmol), tin(IV) chloride in DCM (1.044 M, 1.00 ml, 1.044 mmol) and benzaldehyde in DCM (4.16 M, 250 µl, 1.044 mmol), with chromatography using petrol : ether (3 : 1) as eluent, gave the title compound **7** (257 mg, 83%) as a colourless oil, a 97 : 3 mixture of epimers, $[\alpha]_D$ −88 (*c* = 0.36); (Found: M^+ + NH_4, 314.2108. $C_{20}H_{28}NO_2$ requires *M*, 314.2120); ν_{max}/cm^{-1} 3422, 2958, 2926, 1454, 1090, 1029, 913, 877, 740 and 700; δ_H (300 MHz, $CDCl_3$) major epimer **7**, 0.91 (3 H, d, *J* 7.5, 5-CH_3), 2.39 (1 H, m, 2-H), 2.60 (1 H, dt, *J* 13, 9.5, 2-H′), 2.88 (1 H, m, 5-H), 3.16 (1 H, t, *J* 8.5, 6-H), 3.35 (1 H, dd, *J* 8.5, 5.5, 6-H′), 3.42 (1 H, br s, OH), 4.56 (2 H, s, $PhCH_2$), 4.68 (1 H, dd, *J* 8, 3.5, 1-H), 5.36 (1 H, t, *J* 10, 4-H), 5.58 (1 H, td, *J* 10, 6, 3-H) and 7.30–7.40 (10 H, m, ArH); minor epimer **8**, 0.95 (3 H, d, *J* 7.5, 5-CH_3), 4.50 (2 H, s, $PhCH_2$); δ_C (75 MHz, $CDCl_3$) 17.4, 32.5, 38.7, 73.2, 73.5, 74.9, 125.9, 126.4, 127.4, 127.9, 128.1, 128.5, 128.6, 136.9, 138.2 and 145.0; *m*/*z* (CI, NH_3) 314 (M^+ + 18, 36%), 296 (M^+, 10) and 279 (M^+ − 17, 100).

(1*S*,5*R*,3*Z*)-1-[(*R*)-2-Acetoxy-2-phenylacetoxy]-6-benzyloxy-5-methyl-1-phenylhex-3-ene 9

Following the general procedure, the alcohol **7** (25 mg, 0.084 mmol) and (*R*)-2-acetoxy-2-phenylacetic acid, after chromatography using petrol : ether (3 : 1) as eluent, gave the title compound **9** (33 mg, 83%) as a colourless oil, $[\alpha]_D$ −95 (*c* = 0.37) (Found: M^+ + NH_4, 490.2597. $C_{30}H_{36}NO_5$ requires *M*, 490.2593); ν_{max}/cm^{-1} 2924, 1744, 1453, 1371, 1229, 1206, 1173, 1056 and 735; δ_H (300 MHz, $CDCl_3$) 0.78 (3 H, d, *J* 7, 5-CH_3), 2.13 (3 H, s, O_2CCH_3), 2.42–2.68 (3 H, m, 5-H and 2-H_2), 3.12 (2 H, d, *J* 8, 6-H_2), 4.43 (2 H, s, $PhCH_2$), 5.03 (1 H, dt, *J* 10.5, 7, 3-H), 5.12 (1 H, dd, *J* 10.5, 9.5, 4-H), 5.75 (1 H, t, *J* 7, 1-H), 5.95 (1 H, s, 2′-H) and 7.20–7.50 (15 H, m, ArH); *m*/*z* (CI, NH_3) 490 (M^+ + 18, 100%), 296 (17) and 279 (42).

(1*S*,5*R*,3*Z*)-1-[(*S*)-2-Acetoxy-2-phenylacetoxy]-6-benzyloxy-5-methyl-1-phenylhex-3-ene 10

Following the general procedure, the alcohol **7** (25 mg, 0.084 mmol) and (*S*)-2-acetoxy-2-phenylacetic acid, after chromatography using petrol : ether (3 : 1) as eluent, gave the title compound **10** (35 mg, 88%) as a colourless oil; $[\alpha]_D$ −1.5 (*c* = 0.48); (Found: M^+ + NH_4, 490.2581. $C_{30}H_{36}NO_5$ requires *M*, 490.2593); ν_{max}/cm^{-1} 2854, 1745, 1454, 1372, 1232, 1207, 1175, 1058 and 738; δ_H (300 MHz, $CDCl_3$) 0.83 (3 H, d, *J* 7, 5-CH_3), 2.19 (3 H, s, O_2CCH_3), 2.49–2.73 (3 H, m, 5-H and 2-H_2), 3.15–3.28 (2 H, m, 6-H_2), 4.48 (2 H, s, $PhCH_2$), 5.22–5.36 (2 H, m, 3-H and 4-H), 5.73 (1 H, t, *J* 7, 1-H), 5.99 (1 H, s, 2′-H) and 6.90–7.40 (15 H, m, ArH); *m*/*z* (CI, NH_3) 490 (M^+ + 18, 100%), 296 (17) and 279 (39).

(1*S*,5*R*,3*Z*)-1-Acetoxy-6-benzyloxy-5-methyl-1-phenylhex-3-ene 11

Triethylamine (182 mg, 1.802 mmol), 4-*N*,*N*-dimethylaminopyridine (4 mg, 0.033 mmol) and acetic anhydride (65 mg, 0.637 mmol) were added to the alcohol **7** (103 mg, 0.348 mmol) in DCM (2 ml) and the solution stirred for 50 h. DCM (20 ml) and water (20 ml) were added and the organic phase was washed with dilute aqueous hydrogen chloride (3.5 M, 15 ml) and brine (15 ml) then dried ($MgSO_4$). Concentration under reduced pressure and chromatography of the residue using petrol : ether (3 : 1) as eluent, gave the title compound **11** (105 mg, 89%) as a colourless oil, $[\alpha]_D$ −68 (*c* = 0.50); (Found: M^+ + NH_4, 356.2227. $C_{22}H_{30}NO_3$ requires *M*, 356.2226; ν_{max}/cm^{-1} 2854, 1744, 1372, 1234, 1092, 1028 and 738; δ_H (300 MHz, $CDCl_3$) 0.86 (3 H, d, *J* 7, 5-CH_3), 2.05 (3 H, s, O_2CCH_3), 2.52–2.78 (3 H, m, 5-H and 2-H_2), 3.18–3.29 (2 H, m, 6-H_2), 4.48 (2 H, s, $PhCH_2$), 5.23–5.36 (2 H, m, 3-H and 4-H), 5.76 (1 H, t, *J* 7, 1-H) and 7.25–7.40 (10 H, m, ArH); δ_C (75 MHz, $CDCl_3$) 17.7, 21.4, 32.7, 34.8, 73.1, 75.2, 75.7, 124.3, 126.8, 127.6, 127.7, 128.1, 128.5, 128.5, 135.8, 138.8, 140.4 and

170.4; *m/z* (CI, NH_3) 356 (M^+ + 18, 37%), 296 (25), 279 (75) and 85 (100).

Ozone was bubbled through a solution of acetate **11** (103 mg, 0.308 mmol) in chloroform (10 ml) at –60 °C for 30 min. The solution was purged with oxygen for 10 min, dimethyl sulfide (191 mg, 3.08 mmol) was added and the solution was allowed to warm to room temperature. Following concentration under reduced pressure, the residual oil was dissolved in DCM (5 ml) and added dropwise to a suspension of sodium borohydride (100 mg, 2.63 mmol) in methanol (5 ml) at 0 °C. After 3 h at room temperature, dilute aqueous hydrogen chloride (1 M, 5 ml) was added at 0 °C. Upon warming to room temperature, DCM (25 ml) and water (25 ml) were added, and the aqueous phase was extracted with DCM (25 ml). The organic extracts were washed with brine (30 ml), dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the residue using petrol : ether (1 : 1) as eluent gave a mixture of 3-benzyloxy-2-methylpropanol **16** and (*S*)-3-acetoxy-1-phenylpropan-1-ol (*S*)-**15** (2 : 1, 42 mg), and (*S*)-3-acetoxy-3-phenylpropan-1-ol (*S*)-**14** (17 mg, 29%), as a colourless oil, $[\alpha]_D$ –79 {*c* = 0.61; lit.[1a] for (*R*)-**14**, $[\alpha]_D$ +79.2} (Found: M^+ + NH_4, 212.1294. $C_{11}H_{18}NO_3$ requires *M*, 212.1287); ν_{max}/cm^{-1} 3415, 2956, 1736, 1374, 1240, 1048 and 760; δ_H (300 Mhz, $CDCl_3$) 1.98–2.18 (5 H, m, 2-H_2 and O_2CCH_3), 3.65 (2 H, dd, *J* 7, 5 Hz, 1-H_2), 5.96 (1 H, dd, *J* 9, 5, 3-H) and 7.25–7.40 (5 H, m, ArH); δ_C (75 MHz, $CDCl_3$) 21.4, 39.7, 59.0, 73.4, 126.6, 128.3, 128.8, 140.4 and 171.1; *m/z* (CI, NH_3) 212 (M^+ + 18, 100%), 152 (95) and 134 (98).

(1*S*,5*R*,3*Z*)-6-Benzyloxy-1-[(*R*)-2-methoxy-2-phenyl-3,3,3-trifluoropropanoyloxy]-5-methyl-1-phenylhex-3-ene 12

Following the general procedure, alcohol **7** (31 mg, 0.105 mmol) and (*S*)-2-methoxy-2-phenyl-3,3,3-trifluoropropanoyl chloride gave the title compound **12** (46 mg, 86%) as a colourless oil, $[\alpha]_D$ –14 (*c* = 0.48) (Found: M^+ + NH_4, 530.2498. $C_{30}H_{35}F_3NO_4$ requires *M*, 530.2518); ν_{max}/cm^{-1} 2928, 2851, 1749, 1454, 1272, 1170, 1017 and 762; δ_H (300 MHz, $CDCl_3$) 0.84 (3 H, d, *J* 7, 5-CH_3), 2.57–2.83 (3 H, m, 5-H and 2-H_2), 3.21 (2 H, d, *J* 7.5, 6-H_2), 3.53 (3 H, s, OCH_3), 4.46 (2 H, s, $PhCH_2$), 5.30–5.37 (2 H, m, 3-H and 4-H), 5.91 (1 H, t, *J* 7, 1-H) and 7.20–7.45 (15 H, m, ArH); δ_F (470 MHz, $CDCl_3$) –73.0, –73.2, ratio 9 : 91; *m/z* (CI, NH_3) 530 (M^+ + 18, 92%), 279 (87), 189 (69) and 85 (100).

(1*S*,5*R*,3*Z*)-6-Benzyloxy-1-[(*S*)-2-methoxy-2-phenyl-3,3,3-trifluoropropanoyloxy]-5-methyl-1-phenylhex-3-ene 13

Following the general procedure, alcohol **7** (26 mg, 0.088 mmol) and (*R*)-2-methoxy-2-phenyl-3,3,3-trifluoropropanoyl chloride, after chromatography using petrol : ether (3 : 1) as eluent, gave the title compound **13** (23 mg, 51%) as a colourless oil, $[\alpha]_D$ –70 (*c* = 0.83) (Found: M^+ + NH_4, 530.2528. $C_{30}H_{35}F_3NO_4$ requires *M*, 530.2518); ν_{max}/cm^{-1} 2851, 1748, 1454, 1271, 1170, 1121, 1018 and 718; δ_H (300 MHz, $CDCl_3$) 0.83 (3 H, d, *J* 7, 5-CH_3), 2.56–2.78 (3 H, m, 5-H and 2-H_2), 3.16 (2 H, d, *J* 6.5, 6-H_2), 3.46 (3 H, s, OCH_3), 4.46 (2 H, s, $PhCH_2$), 5.16–5.25 (2 H, m, 3-H and 4-H), 5.98 (1 H, t, *J* 7, 1-H) and 7.30–7.50 (15 H, m, ArH); δ_F (470 MHz, $CDCl_3$) –73.0, –73.2, ratio 95 : 5; *m/z* (CI, NH_3) 530 (M^+ + 18, 55%) and 279 (100).

O-[(5*R*,2*E*)-5-*tert*-Butyldimethylsilyloxyhex-2-en-1-yl] *S*-methyl dithiocarbonate 70

Allylic alcohol **69** (2.98 g, 12.96 mmol) in benzene (15 ml) was added to sodium hydride (571 mg, a 60% dispersion in mineral oil, 14.27 mmol) in benzene (12.5 ml) at room temperature. After 2 h at 40 °C, carbon disulfide (3.94 g, 51.84 mmol) was added at 5 °C and the mixture was stirred at room temperature for 3 h. Methyl iodide (7.37 g, 51.90 mmol) was added at 5 °C and the mixture stirred for 15 h at room temperature. The mixture was filtered through celite and the filtercake was washed with DCM (100 ml). The organic extracts were washed with brine (75 ml), dried ($MgSO_4$) and concentrated under reduced pressure to yield the title compound **70** (3.82 g, 92%) as a yellow oil, $[\alpha]_D$ –4.7 (*c* = 0.80) (Found: M^+ + H, 321.1389. $C_{14}H_{29}O_2S_2Si_2$ requires *M*, 321.1378; ν_{max}/cm^{-1} 2929, 1254, 1217, 1185, 1059, 836 and 775; δ_H (300 MHz, C_6D_6) 0.07 [6 H, s, $Si(CH_3)_2$], 1.04 [9 H, s, $SiC(CH_3)_3$], 1.07 (3 H, d, *J* 6, 6-H_3), 1.97–2.18 (2 H, m, 4-H_2), 2.22 (3 H, s, SCH_3), 3.68 (1 H, m, 5-H), 5.02 (2 H, d, *J* 6.5, 1-H_2) and 5.56 and 5.72 (each 1 H, dt, *J* 15.5, 6.5, 2-H or 3-H); δ_C (75 MHz, C_6D_6) –4.6, –4.4, 18.2, 18.8, 23.6, 26.0, 42.8, 68.2, 74.2, 125.3, 134.5 and 216.0; *m/z* (CI, NH_3) 321 (M^+ + 1, 63%), 189 (97), 159 (100) and 132 (84).

S-[(3*RS*,5*R*)-5-*tert*-Butyldimethylsilyloxyhex-1-en-3-yl] *S*′-methyl dithiocarbonate 71

Xanthate **70** (3.82 g, 11.93 mmol) was heated under reflux in toluene (120 ml) for 15 h. Concentration under reduced pressure gave the title compound **71** (3.82 g, 100%) as a yellow oil, a 1 : 1 mixture of epimers (Found: M^+ + H, 321.1376. $C_{14}H_{29}O_2S_2Si_2$ requires M, 321.1378); ν_{max}/cm^{-1} 2930, 1649, 1255, 1047, 865, 836 and 775; δ_H (300 MHz, $CDCl_3$) 0.05 and 0.06 (each 3 H, s, $SiCH_3$), 0.89 and 0.91 [each 4.5 H, s, $SiC(CH_3)_3$], 1.16 (3 H, d, *J* 6, 6-H_3), 1.64–1.88 (2 H, m, 4-H_2), 2.41 and 2.42 (each 1.5 H, s, SCH_3), 3.89 (1 H, m, 5-H), 4.29 (1 H, m, 3-H), 5.06–5.32 (2 H, m, 1-H_2) and 5.80 (1 H, m, 2-H); δ_C (75 MHz, $CDCl_3$) -4.8, –4.6, –4.2, –4.0, 12.9, 13.0, 18.0, 23.8, 24.0, 25.9, 25.9, 29.7, 43.2, 43.8, 45.1, 45.8, 65.7, 66.0, 115.9, 116.9, 137.4, 138.0, 188.5 and 188.6; *m/z* (CI, NH_3) 321 (M^+ + 1, 26%) and 189 (100).

(*R*)-5-*tert*-Butyldimethylsilyloxyhex-2-enyl(tributyl)stannane 72

Tributyltin hydride (2.27 g, 7.81 mmol) and α-azo-bis-*iso*-butyronitrile (51 mg, 0.311 mmol) were added to a degassed solution of the dithiocarbonate **71** (2.0 g, 6.25 mmol) in benzene (85 ml) and the solution was heated to reflux for 3.5 h. Following concentration under reduced pressure, chromatography of the residue using petrol (with 2% triethylamine) as eluent afforded the title compound **72** (2.66 g, 85%) as a colourless oil, a 2 : 1 mixture of (*E*)- and (*Z*)-isomers, $[\alpha]_D$ +2.3 (*c* = 1.16) (Found: $M^+ - C_4H_9$, 447.2109. $C_{20}H_{43}OSi^{120}Sn$ requires *M*, 447.2104); ν_{max}/cm^{-1} 2928, 1463, 1376, 1254, 1129, 1090, 1004, 836 and 775; δ_H (300 MHz, $CDCl_3$) 0.05 and 0.07 (each 3 H, s, $SiCH_3$), 0.84–0.94 [24 H, m, 3 × $SnCH_2CH_2CH_2CH_3$ and $SiC(CH_3)_3$], 1.11 (2 H, d, *J* 6, 6-H_3), 1.13 (1 H, d, *J* 6, 6-H_3), 1.24–1.74 (14 H, m, 3 × $SnCH_2CH_2CH_2CH_3$ and 1-H_2), 1.98–2.23 (2 H, m, 4-H_2), 3.73 (0.66 H, m, 5-H), 3.81 (0.34 H, m, 5-H), 5.08 (0.33 H, dt, *J* 10.5, 7, 2-H), 5.18 (0.67 H, dt, *J* 15, 7, 2-H) and 5.57 (1 H, m, 3-H); δ_C (75 MHz, $CDCl_3$) –4.6, –4.5, 9.2, 9.4, 10.7, 13.7, 14.4, 18.2, 23.2, 23.5, 25.9, 27.3, 29.1,

37.4, 43.3, 69.0, 69.4, 120.5, 122.0, 129.7 and 131.5; *m/z* (EI) 447 ($M^+ - 57$, 86%), 445 ($M^+ - 57$, 70) and 291 (100).

(*R*)-5-Hydroxyhex-2-enyl(tributyl)stannane 73

Tetrabutylammonium fluoride in THF (1 M, 10.4 ml, 10.4 mmol) was added to the silyl ether **72** (3.39 g, 6.74 mmol) in THF (10 ml) and was stirred at room temperature for 15 h. Water (20 ml) was added and the mixture was stirred for a further 1 h. The mixture was extracted with ether (4 × 20 ml) and the organic extracts were washed with brine (75 ml), dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the residue using petrol : ether (10 : 1 + 1% triethylamine) as solvent, gave the title compound **73** (2.31 g, 88%) as a colourless oil, a 2 : 1 mixture of (*E*)- and (*Z*)-isomers), $[\alpha]_D$ +2.3 (*c* = 0.70) (Found: $M^+ - C_4H_9$, 333.1236. $C_{14}H_{29}O^{120}Sn$ requires *M*, 333.1239); ν_{max}/cm^{-1} 3351, 2925, 1463, 1376, 1073 and 961; δ_H (300 Mz, $CDCl_3$) 0.76–0.95 (15 H, m, 3 × Sn$CH_2CH_2CH_2CH_3$), 1.18 (2 H, d, *J* 6.5, 6-H_3), 1.22 (1 H, d, *J* 6, 6-H_3), 1.25–1.87 (14 H, m, 3 × Sn$CH_2CH_2CH_2CH_3$ and 2-H_2), 2.00–2.26 (2 H, m, 4-H_2), 3.72 (0.7 H, m, 5-H), 3.81 (0.3 H, m, 5-H), 5.16 and 5.69 (each 1 H, m, 2-H or 3-H); δ_C (75 MHz, $CDCl_3$) 9.2, 9.4, 10.8, 13.7, 14.5, 22.5, 22.8, 27.3, 29.1, 36.9, 42.8, 67.5, 67.9, 119.2, 120.8, 132.0 and 133.8; *m/z* (EI) 333 ($M^+ - 57$, 1%), 331 $M^+ - 57$, 1), (291 (9), 269 (17), 135 (43) and 84 (100).

(*R*)-5-Methoxyhex-2-enyl(tributyl)stannane 74

Hydroxyalkenylstannane **73** (516 mg, 1.326 mmol) in THF (5 ml) was added to a suspension of sodium hydride (64 mg of a 60% dispersion in mineral oil, 1.60 mmol) in THF (1 ml) at room temperature. After 2 h at 35 °C, methyl iodide (941 mg, 6.630 mmol) was added at room temperature and the suspension was stirred for 15 h. Water (5 ml) was added and the mixture was extracted with ether (4 × 15 ml). The organic extracts were washed with brine (50 ml), dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the residue using petrol : ether (40 : 1 + 1% triethylamine) gave the title compound **74** (452 mg, 85%) as a colourless oil, a 2 : 1 mixture of the (*E*)- and (*Z*)-isomers, $[\alpha]_D$ +7.3 (*c* = 1.90) (Found: $M^+ - C_4H_9$, 347.1398. $C_{15}H_{31}O^{120}Sn$ requires *M*, 347.1397); ν_{max}/cm^{-1} 2925, 1463, 1376, 1129, 1099 and 960; δ_H (300 MHz, $CDCl_3$) 0.75–0.96 (15 H, m, 3 × Sn$CH_2CH_2CH_2CH_3$), 1.11 (2 H, d, *J* 6, 6-H_3), 1.14 (1 H, d, *J* 6, 6-H_3), 1.22–1.84 (14 H, m, 3 × Sn$CH_2CH_2CH_2CH_3$ and 1-H_2), 1.98–2.35 (2 H, m, 4-H_2), 3.25 (1 H, m, 5-H), 3.31 (2 H, s, OCH_3), 3.33 (1 H, s, OCH_3), 5.08 (0.34 H, dt, *J* 10.5, 7, 2-H), 5.18 (0.66 H, dt, *J* 15, 7.5, 2-H) and 5.60 (1 H, m, 3-H); δ_C (75 MHz, $CDCl_3$) 9.2, 9.4, 10.7, 13.7, 14.4, 18.8, 19.1, 27.3, 29.1, 33.6, 39.4, 55.9, 56.0, 77.4, 119.7, 121.3, 130.2 and 131.8; *m/z* (EI) 347 ($M^+ - 57$, 13%), 345 ($M^+ - 57$, 9), 291 (20), 269 (11) and 59 (100).

(*R*)-5-Hydroxyhexyl(tributyl)stannane 75

Toluene 4-sulfonyl hydrazide (239 mg, 1.28 mmol) and then sodium acetate (105 mg, 1.28 mmol) were added to the allylstannane **73** (100 mg, 0.257 mmol) in ethanol (10 ml) and the solution was heated under reflux. After 2 h, further portions of toluene 4-sulfonyl hydrazide (239 mg, 1.28 mmol) and sodium acetate (105 mg, 1.28 mmol) were added and the solution was heated under reflux for a further 2 h. Following concentration under reduced pressure, hexane (25 ml) and water (25 ml) were added. The organic phase was washed with brine (20 ml), dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the residue using petrol : ether (5 : 1 + 1% triethylamine) as the eluent, gave the title compound **75** (83 mg, 83%) as a colourless oil, $[\alpha]_D$ −3.7 (*c* = 0.86) (Found: $M^+ - C_4H_9$, 335.1393. $C_{14}H_{31}O^{120}Sn$ requires *M*, 335.1396); ν_{max}/cm^{-1} 3339, 2925, 1462, 1376 and 1072; δ_H (300 MHz, $CDCl_3$) 0.74–0.97 (17 H, m, 1-H_2 and 3 × Sn$CH_2CH_2CH_2CH_3$), 1.22 (3 H, d, *J* 6, 6-H_3), 1.25–1.65 (18 H, m, 2-H_2, 3-H_2, 4-H_2 and 3 × Sn$CH_2CH_2CH_2CH_3$) and 3.83 (1 H, m, 5-H); δ_C (75 MHz, $CDCl_3$) 8.8, 9.0, 13.7, 23.5, 27.1, 27.4, 29.3, 30.5, 39.0 and 68.2; *m/z* (EI) 335 ($M^+ - 57$, 100%), 333 ($M^+ - 57$, 80) and 177 (74).

(*R*)-5-[(*R*)-2-Methoxy-2-phenyl-3,3,3-trifluoropropanonyloxy]hexyl(tributyl)stannane 76

Following the general procedure, alcohol **75** (14 mg, 0.036 mmol) and (*S*)-2-methoxy-2-phenyl-3,3,3-trifluoropropanoyl chloride afforded the title compound **76** (22 mg, 100%) as a colourless oil, $[\alpha]_D$ +14.5 (*c* = 0.94) (Found: $M^+ - C_4H_9$, 551.1794. $C_{24}H_{38}F_3O_3{}^{120}Sn$ requires *M*, 551.1794); ν_{max}/cm^{-1} 2925, 1746, 1454, 1270, 1170, 1123, 1020 and 716; δ_H (500 MHz, C_6D_6) 0.86–1.10 (15 H, m, 3 × Sn$CH_2CH_2CH_2CH_3$), 1.12 (3 H, d, *J* 6, 6-H_3), 1.30–1.76 (20 H, m, 3 × Sn$CH_2CH_2CH_2CH_3$ and 1-H_2, 2-H_2, 3-H_2 and 4-H_2), 3.57 (3 H, s, OCH_3), 5.19 (1 H, m, 5-H), 7.13–7.24 (3 H, m, ArH) and 7.80–7.84 (2 H, m, ArH); δ_F (470 MHz, C_6D_6) −73.0; *m/z* (EI) 551 ($M^+ - 57$, 21%), 549 ($M^+ - 57$, 15) and 317 (100).

(*R*)-5-[(*S*)-2-Methoxy-2-phenyl-3,3,3-trifluoropropionyloxy]-hexyl(tributyl)stannane 77

Following the general procedure, alcohol **75** (37 mg, 0.095 mmol) and (*R*)-2-methoxy-2-phenyl-3,3,3-trifluoropropanoyl chloride afforded the title compound **77** (40 mg, 70%) as a colourless oil, $[\alpha]_D$ −36.5 (*c* = 1.62) (Found: $M^+ - C_4H_9$, 551.1788. $C_{24}H_{38}F_3O_3{}^{120}Sn$ requires *M*, 551.1794); ν_{max}/cm^{-1} 2925, 1746, 1454, 1270, 1169, 1123, 1081, 1021 and 715; δ_H (500 MHz, C_6D_6) 0.86–1.08 (15 H, m, 3 × Sn$CH_2CH_2CH_2CH_3$), 1.16 (3 H, d, *J* 6, 6-H_3), 1.20 – 1.75 (20 H, m, 3 × Sn$CH_2CH_2CH_2CH_3$ and 1-H_2, 2-H_2, 3-H_2 and 4-H_2), 3.57 (3 H, s, OCH_3), 5.20 (1 H, m, 5-H), 7.14–7.23 (3 H, m, ArH) and 7.80–7.84 (2 H, m, ArH); δ_F (470 MHz, C_6D_6) −72.9; *m/z* (CI, NH_3) 551 ($M^+ - 57$, 7%), 549 ($M^+ - 57$, 5), 308 (56) and 30 (100).

(1*R*,6*R*,3*Z*)-6-Methoxy-1-phenylhept-3-en-1-ol 78

Following the general procedure, stannane **74** (450 mg, 1.12 mmol), tin(IV) bromide (1.044 M in DCM, 1.07 ml, 1.12 mmol) and benzaldehyde (321 µl, 1.12 mmol), after chromatography using petrol : ether (2 : 1) as eluent, gave the title compound **78** (193 mg, 78%) as a colourless oil, a 91 : 9 mixture of epimers, $[\alpha]_D$ +95 (*c* = 0.90) (Found: $M^+ - OH$, 203.1434. $C_{14}H_{18}O$ requires *M*, 203.1436); ν_{max}/cm^{-1} 3417, 2972, 1493, 1453, 1135, 1086, 1054, 760 and 701; δ_H (300 MHz, $CDCl_3$) 1.16 (3 H, d, *J* 6, 7-H_3), 2.12 (1 H, dt, *J* 14, 5, 2- or 5-H), 2.30–2.50 (2 H, m, 2 × 2- or 5-H), 2.58 (1 H, m, 2- or 5-H), 3.15 (1 H, br s, OH), 3.25–3.40 (4 H, m, 6-H and OCH_3), 4.71 (1 H, dd, *J* 8.5, 4.5, 1-H), 5.50–5.66 (2 H, m, 3-H and 4-H) and 7.23–7.39 (5 H, m, ArH); δ_C (75 MHz, $CDCl_3$) major epimer **78** 18.9, 34.5, 37.8, 56.1, 73.5, 76.5, 125.8, 127.3, 127.4, 128.3, 129.3 and 144.6; minor epimer **81** 18.6, 34.0

and 37.3; *m/z* (CI, NH_3) 238 (M^+ + 18, 1%), 220 (M^+, 9), 203 (M^+ – 17, 96), 171 (98), 121 (66) and 59 (100).

(1*R*,6*R*,3*Z*)-6-Methoxy-1-(4-nitrobenzoyloxy)-1-phenylhept-3-ene 79

Triethylamine (27 mg, 0.27 mmol), 4-*N*,*N*-dimethylaminopyridine (2 mg, 0.016 mmol) and 4-nitrobenzoyl chloride (59 mg, 0.318 mmol) were added to the alcohol **78** (23 mg, 0.105 mmol) in DCM (2 ml) and the mixture stirred at room temperature for 72 h. Ether (20 ml) and water (20 ml) were added, and the organic phase was washed with aqueous hydrogen chloride (3.5 M, 15 ml) and brine (15 ml) then dried ($MgSO_4$). After concentration under reduced pressure, chromatography of the residue using petrol ether (4 : 1) as eluent gave the title compound **79** (34 mg, 88%) as a colourless oil, $[\alpha]_D$ −18 (*c* = 1.58 (Found: $M^+ + NH_4$, 387.1914. $C_{21}H_{27}N_2O_5$ requires *M*, 387.1919); ν_{max}/cm^{-1} 2972, 1725, 1607, 1529, 1345, 1273, 1102 and 720; δ_H (300 MHz, $CDCl_3$) 1.11 (3 H, d, *J* 6 7-H_3), 2.16 and 2.29 (each 1 H, dt, *J* 14.5, 7, 5-H), 2.75 and 2.92 (each 1 H, dt, *J* 14.5, 7, 2-H), 3.28 (1 H, m, 6-H), 3.33 (3 H, s, OCH_3), 5.47–5.62 (2 H, m, 3-H and 4-H), 6.06 (1 H, t, *J* 7, 1-H), 7.31–7.49 (5 H, m, ArH) and 8.23–8.36 (4 H, m, ArH); δ_C (75 MHz, $CDCl_3$), 18.9, 34.1, 34.5, 56.1, 76.4, 77.3, 123.5, 125.2, 126.6, 128.3, 128.6, 129.4, 130.8, 135.8, 139.6, 150.6 and 163.9; *m/z* (CI, NH_3) 387 (M^+ + 18, 8%), 203 (100) and 171 (56).

(1*R*,6*R*,3*Z*)-1-Acetoxy-6-methoxy-1-phenylhept-3-ene 80

Triethylamine (402 mg, 3.98 mmol), 4-*N*,*N*-dimethylaminopyridine (5 mg, 0.041 mmol) and acetic anhydride (162 mg, 1.59 mmol) were added to the alcohol **78** (175 mg, 0.795 mmol) in DCM (4 ml) and the mixture stirred at room temperature for 15 h. DCM (35 ml) and water (35 ml) were added, and the organic phase washed with aqueous hydrogen chloride (3.5 M, 25 ml), saturated aqueous sodium hydrogen carbonate (25 ml) and brine (15 ml) then dried ($MgSO_4$). After concentration under reduced pressure, chromatography of the residue using petrol : ether (3 : 1) as eluent gave the title compound **80** (192 mg, 92%) as a colourless oil, $[\alpha]_D$ +34 (*c* = 0.7); Found: $M^+ + NH_4$, 280.1917. $C_{16}H_{26}NO_3$ requires *M*, 280.1913); ν_{max}/cm^{-1} 2972, 1741, 1373, 1237, 1094, 1024 and 700; δ_H (300 MHz, C_6D_6) 1.07 (3 H, d, *J* 6, 7-H_3), 1.74 (3 H, s, O_2CCH_3), 2.12, 2.31, 2.56 and 2.76 (each 1 H, dt, *J* 14, 7, 2-H or 5-H), 3.12 (1 H, m, 6-H), 3.16 (3 H, s, OCH_3), 5.50 and 5.63 (each 1 H, m, 3- or 4-H), 6.02 (1 H, t, *J* 7, 1-H), and 7.10–7.37 (5 H, m, ArH); δ_C (75 MHz, C_6D_6) 19.1, 20.7, 34.4, 34.8, 55.8, 75.5, 76.6, 125.9, 127.0, 128.6, 129.3, 140.9 and 169.4; *m/z* (CI, NH_3) 280 M^+ + 18, 50%), 220 (71), 203 (100) and 171 (100).

Ozone was bubbled through a solution of the acetoxyalkene **80** (100 mg, 0.382 mmol) in chloroform (5 ml) at −78 °C for 15 min. The solution was purged with oxygen for 10 min, then dimethyl sulfide (170 mg, 2.73 mmol) was added and the mixture allowed to warm to room temperature. After concentration under reduced pressure, the residual oil was dissolved in DCM (2 ml), and methanol (2 ml) and sodium borohydride (100 mg, 2.63 mmol) were added at 0 °C. After 1.5 h at room temperature aqueous hydrogen chloride (1 M, 4 ml) was added at 0 °C. After warming to room temperature DCM (25 ml) and water (25 ml) were added, and the aqueous phase was extracted with DCM (25 ml). The organic extracts were washed with brine (30 ml), dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the residue using petrol : ether (2 : 1 to 1 : 2) as eluent gave (*R*)-1-phenyl-3-acetoxypropan-1-ol (*R*)-**15** (11 mg, 15%) as a colourless oil, $[\alpha]_D$ +15 (*c* = 0.49) (Found: M^+, 194.0943. $C_{11}H_{14}O_3$ requires *M*, 194.0943); ν_{max}/cm^{-1} 3438, 2957, 1738, 1368, 1243, 1041 and 702; δ_H (300 MHz, $CDCl_3$) 2.01–2.45 (6 H, m, O_2CCH_3, 2-H_2 and OH), 4.16 (1 H, dt, *J* 11.5, 5.5, 3-H), 4.35 (1 H, ddd, *J* 11.5, 7.5, 5.5, 3-H′), 4.83 (1 H, dd, *J* 8, 5.5, 1-H) and 7.30–7.42 (5 H, m, ArH); δ_C (75 MHz, $CDCl_3$) 21.0, 38.0, 61.6, 71.3, 125.8, 127.8, 128.6, 143.9 and 171.3; *m/z* (CI, NH_3) 212 (M^+ + 18, 4%), 193 (M^+ − 1, 7) and 177 (M^+ − 17, 100). The second fraction contained (*R*)-3-acetoxy-3-phenylpropan-1-ol (*R*)-**14** (43 mg, 58%) as a colourless oil, $[\alpha]_D$ +69 (*c* = 1.35; lit.[1a,9] +79.2), all other data as for the (*S*)-enantiomer (*S*)-**14** prepared earlier.

(1*S*,6*R*,3*Z*)-6-Methoxy-1-phenylhept-3-en-1-ol 81

Sodium hydroxide (57 mg, 1.43 mmol) was added to the 4-nitrophenyl ester **86** (80 mg, 0.216 mmol) in methanol (6 ml). After 2 h at room temperature water (15 ml) was added and the mixture extracted with ether (2 × 20 ml). The organic extracts were washed with brine (30 ml), dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the residue using petrol : ether (2 : 1) as eluent gave the title compound **81** (40 mg, 84%) as a colourless oil, $[\alpha]_D$ −72 (*c* = 1.78) (Found: M^+, 220.1461. $C_{14}H_{20}O_2$ requires *M*, 220.1463); ν_{max}/cm^{-1} 3422, 3126, 2972, 1494, 1453, 1378, 1199, 1135, 1087, 1052, 760 and 702; δ_H (300 MHz, $CDCl_3$) 1.18 (3 H, d, *J* 6.5, 7-H_3), 2.28 (2 H, t, *J* 6.5, 5-H_2), 2.58 (2 H, t, *J* 6.5, 2-H_2), 3.09 (1 H, br s, OH), 3.31–3.42 (4 H, m, 6-H and OCH_3), 4.78 (1 H, t, *J* 6.5, 1-H), 5.53 (1 H, dt, *J* 11, 7, 3-H), 5.64 (1 H, dt, *J* 11, 7, 4-H) and 7.26–7.42 (5 H, m, ArH); δ_C (75 MHz, $CDCl_3$) major epimer **81** 18.6, 34.0, 37.3, 56.1, 73.4, 76.4, 125.8, 127.1, 127.3, 128.3, 128.8 and 144.5; minor epimer **78** 18.9, 34.5 and 37.8; *m/z* (CI, NH_3) 238 (M^+ + 18, 38%), 220 (M^+, 33) and 203 (100).

(1*R*,6*R*,3*Z*)-6-Methoxy-1-[(*R*)-2-methoxy-2-phenyl-3,3,3-trifluoropropanoyloxy]-1-phenylhept-3-ene 82

Following the general procedure, alcohol **78** (16 mg, 0.072 mmol) and (*S*)-2-methoxy-2-phenyl-3,3,3-trifluoropropanoyl chloride afforded the title compound **82** (31 mg, 97%) as a colourless oil, $[\alpha]_D$ +52 (*c* = 1.35) (Found: $M^+ + NH_4$, 454.2201. $C_{24}H_{31}F_3NO_4$ requires *M*, 454.2205); ν_{max}/cm^{-1} 2967, 1748, 1261, 1170, 1095, 1018, 801 and 700; δ_H (300 MHz, $CDCl_3$) 1.08 (3 H, d, *J* 6, 7-H_3), 2.05 and 2.17 (each 1 H, dt, *J* 14.5, 7, 5-H), 2.62 and 2.76 (each 1 H, dt, *J* 14.5, 7, 2-H), 3.22 (1 H, m, 6-H), 3.31 and 3.49 (each 3 H, s, OCH_3), 5.36 (1 H, m, 3- or 4-H), 5.49 (1 H, dt, *J* 10.5, 7, 3- or 4-H), 6.02 (1 H, dd, *J* 7, 6.5, 1-H) and 7.31–7.48 (10 H, m, ArH); δ_F (470 MHz, $CDCl_3$) −73.0, −73.1, ratio 91 : 9; *m/z* (CI, NH_3) 454 (M^+ + 18, 8%), 203 (100) and 171 (62).

(1*R*,6*R*,3*Z*)-6-Methoxy-1-[(*S*)-2-methoxy-2-phenyl-3,3,3-trifluoropropanoyloxy]-1-phenylhept-3-ene 83

Following the general procedure, alcohol **78** (15 mg, 0.068 mmol) and (*R*)-2-methoxy-2-phenyl-3,3,3-trifluoropropanoyl chloride afforded the title compound **83** (23 mg, 78%) as a colourless oil, $[\alpha]_D$ −4.9 (*c* = 0.93) (Found: $M^+ + NH_4$, 454.2210. $C_{24}H_{31}F_3NO_4$ requires *M*, 454.2205); ν_{max}/cm^{-1} 2972, 1749, 1272, 1170, 1124,

1017, 995, 719 and 699; δ_H (300 MHz, $CDCl_3$) 1.09 (3 H, d, *J* 6, 7-H_3), 2.11 and 2.23 (each 1 H, dt, *J* 14.5, 7, 5-H), 2.64 and 2.82 (each 1 H, dt, *J* 14.5, 7, 2-H), 3.27 (1 H, m, 6-H), 3.32 and 3.58 (each 3 H, s, OCH_3), 5.48 (1 H, m, 3- or 4-H), 5.58 (1 H, dt, *J* 10.5, 7, 3- or 4-H), 5.96 (1 H, dd, *J* 7.5, 6.5, 1-H) and 7.23–7.47 (10 H, m, ArH); δ_F (470 MHz, $CDCl_3$) −73.0, −73.2, ratio 10 : 90; *m*/*z* (CI, NH_3) 454 (M^+ + 18, 19%), 220 (18) and 203 (100).

(1*R*,6*R*,3*Z*)-1-[(*R*)-2-Acetoxy-2-phenylacetoxy]-6-methoxy-1-phenylhept-3-ene 84

Following the general procedure, alcohol **78** (9 mg, 0.041 mmol) and (*R*)-2-acetoxy-2-phenylacetic acid, after chromatography using petrol : ether (2 : 1) as eluent, gave the title compound **84** (13 mg, 80%) as a colourless oil, $[\alpha]_D$ −31 (*c* = 0.53) (Found: M^+ + NH_4, 414.2265. $C_{24}H_{32}NO_5$ requires M, 414.2281); ν_{max}/cm^{-1} 2931, 1747, 1373, 1232, 1208, 1175, 1089, 1056 and 699; δ_H (300 MHz, $CDCl_3$) 1.08 (3 H, d, *J* 6, 7-H_3), 2.07 (1 H, m, 5-H), 2.17 –2.30 (4 H, m, 5-H′ and O_2CCH_3), 2.57 and 2.69 (each 1 H, dt, *J* 14.5, 7, 2-H), 3.24 (1 h, m, 6-H), 3.32 (3 H, s, OCH_3), 5.43 (1 H, m, 3- or 4-H), 5.54 (1 H, dt, *J* 10.5, 7, 3- or 4-H), 5.77 (1 H, t, *J* 7, 1-H), 6.02 (1 H, s, 2′-H) and 6.98–7.55 (10 H, m, ArH); *m*/*z* (CI, NH_3) 414 (M^+ + 18, 4%), 341 (17), 203 (100), 171 (76) and 59 (88).

(1*R*,6*R*,3*Z*)-1-[(*S*)-2-Acetoxy-2-phenylacetoxy]-6-methoxy-1-phenylhept-3-ene 85

Following the general procedure, alcohol **78** (12 mg, 0.055 mmol) and (*S*)-2-acetoxy-2-phenylacetic acid, after chromatography using petrol : ether (4 : 1) as eluent, gave the title compound **85** (19 mg, 87%) as a colourless oil, $[\alpha]_D$ +75 (*c* = 0.90) (Found: M^+ + NH_4, 414.2287. $C_{24}H_{32}NO_5$ requires *M*, 414.2281); ν_{max}/cm^{-1} 2972, 1747, 1373, 1232, 1176, 1089, 1056 and 699; δ_H (300 MHz, $CDCl_3$) 1.04 (3 H, d, *J* 6, 7-H_3), 1.92–2.14 (2 H, m, 5-H_2), 2.21 (3 H, s, O_2CCH_3), 2.42–2.63 (2 H, m, 2-H_2), 3.18 (1 H, m, 6-H), 3.24 (3 H, s, OCH_3), 5.17 (1 H, m, 3- or 4-H), 5.36 (1 H, dt, *J* 11, 7.5, 3- or 4-H), 5.79 (1 H, t, *J* 6.5, 1-H), 6.03 (1 H, s, 2′-H) and 7.18–7.55 (10 H, m, ArH); *m*/*z* (CI, NH_3) 414 (M^+ + 18, 28%) and 203 (100).

(1*S*,6*R*,3*Z*)-6-Methoxy-1-(4-nitrobenzoyloxy)-1-phenylhept-3-ene 86

Diethyl azodicarboxylate (94 mg, 0.540 mmol) was added to a suspension of the alcohol **78** (79 mg, 0.359 mmol), triphenylphosphine (141 mg, 0.538 mmol) and 4-nitrobenzoic acid (90 mg, 0.539 mmol) in toluene (3 ml) at −35 °C and the mixture was allowed to warm to room temperature. After 1.75 h, ether (25 ml) and water (25 ml) were added. The organic phase was washed with brine (20 ml), dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the residue using petrol : ether (6 : 1) as eluent gave the title compound **86** (106 mg, 80%) as a colourless oil, $[\alpha]_D$ +35.5 (*c* = 0.76) (Found: $M^+ + NH_4$, 387.1917. $C_{21}H_{27}N_2O_5$ requires M, 387.1919); ν_{max}/cm^{-1} 2972, 1726, 1607, 1529, 1345, 1273, 1102, 720 and 700; δ_H (300 MHz, $CDCl_3$) 1.12 (3 H, d, *J* 6 7-H_3), 2.16 (1 H, dt, *J* 14, 7, 5-H), 2.30 (1 H, dt, *J* 14.5, 6, 5-H), 2.75 and 2.92 (each 1 H, dt, *J* 14.5, 7, 2-H), 3.28 (1 H, m, 6-H), 3.32 (3 H, s, OCH_3), 5.45–5.63 (2 H, m, 3-H and 4-H), 6.08 (1 H, t, *J* 7, 1-H), 7.32–7.48 (5 H, m, ArH) and 8.24–8.35 (4 H, m, ArH); δ_C (75 MHz, $CDCl_3$), 18.9, 34.1, 34.5, 56.1, 76.4, 77.3, 123.5, 125.3, 126.5, 128.3, 128.6, 129.3, 130.8, 135.8, 139.6, 150.6 and 163.9; *m*/*z* (CI, NH_3) 387 (M^+ + 18, 10%), 203 (100) and 171 (44).

N-Methyl-2-(prop-2-enylthio)imidazole 133

Allyl bromide (10 g, 82.64 mmol) was added dropwise to 2-mercapto-1-methylimidazole (4.71 g, 41.32 mmol) and potassium carbonate (5.70 g, 41.32 mmol) in acetone (100 ml) and the mixture stirred for 3 h. Water (50 ml) was added and the stirring continued for a further 30 min. The mixture was extracted with ether and the organic extracts washed with brine and dried ($MgSO_4$). Following concentration under reduced distillation of the residue at 160 °C, 2 mm Hg, gave the title compound **133** (5.3 g, 83%) as a yellow oil (Found: M^+, 154.0565. $C_7H_{10}N_2S$ requires *M*, 154.0565); ν_{max}/cm^{-1} 3375, 1459, 1413, 1280, 1125, 920, 734 and 688; δ_H (300 MHz, $CDCl_3$) 3.60 (5 H, m, NCH_3, CH_2S), 5.00 (2 H, m, 3′-H_2), 5.90 (1 H, ddt, *J* 17, 10, 7, 2′-H), 6.90 (1 H, d, *J* 1, ArH) and 7.05 (1 H, d, *J* 1, ArH); δ_C (75 MHz, $CDCl_3$) 33.4, 37.8, 118.0, 122.4, 129.4, 133.6 and 140.8; *m*/*z* (EI) 154 (M^+, 100%).

(*S*)-3-*tert*-Butyldimethylsilyloxy-1-iodo-2-methylpropane 135

Methanesulfonyl chloride (12.0 ml, 155.3 mmol) was added dropwise to the alcohol **134** (26.4 g, 129.4 mmol) and triethylamine (36 ml, 259 mmol) in DCM (200 ml) at −20 °C. The mixture was allowed to warm to ambient temperature over 1 h and was then washed with sodium hydroxide (10% w/v) and water then dried ($MgSO_4$). Concentration under reduced pressure gave the corresponding mesylate (36.6 g, 100%) as a colourless oil, $[\alpha]_D$ +4.1 (*c* = 6) (Found: M^+ + H, 283.1401. $C_{11}H_{27}O_4SSi$ requires *M*, 283.1399); ν_{max}/cm^{-1} 2956, 1473, 1358, 1255, 1177, 1094, 1044, 966, 839 and 779; *m*/*z* (CI, NH_3) 300 (M^+ + NH_4, 8%), 283 (M^+ + 1, 100) and 264 (60).

The mesylate (36.49 g, 129.4 mmol) and sodium iodide (58.2 g, 388.2 mmol) in acetone (500 ml) was heated under reflux for 18 h. Following concentration under reduced pressure, the residue was diluted with ethyl acetate and the solution washed with aqueous sodium thiosulfate (5% w/v) and brine then dried ($MgSO_4$). Concentration under reduced pressure and chromatography of the residue using petrol : ether (3 : 1) as eluent gave the title compound **135** (28.46 g, 70%) as a colourless oil, $[\alpha]_D$ +5.6 (*c* = 7.2, CH_2Cl_2) (Found: M^+ + H, 315.0643. $C_{10}H_{24}IOSi$ requires *M*, 315.0641); ν_{max}/cm^{-1} 2956, 2929, 2857, 1471, 1257, 1196, 1103, 839 and 777; δ_H (300 MHz, $CDCl_3$) 0.10 (6 H, s, 2 × CH_3Si), 0.92 [9 H, s, $SiC(CH_3)_3$], 0.98 (3 H, d, *J* 7, 2-CH_3), 1.65 (1 H, m, 2-H), 3.30 (2 H, m, 1-H_2), 3.42 (1 H, dd, *J* 10, 7, 3-H) and 3.55 (1 H, dd, *J* 10, 5, 3-H′); *m*/*z* (CI, NH_3) 315 (M^+ + 1, 100%).

(5*R*)-6-*tert*-Butyldimethylsilyloxy-3-(*N*-methyl-2-imidazol-2-ylthio)-5-methylhex-1-ene 136

Butyllithium in hexanes (1.6 M, 22 ml, 34.98 mmol) was added to the propenyl sulfide **133** (4.90 g, 31.8 mmol) and hexamethylphosphoric triamide (11.4 ml, 63.6 mmol) in THF (150 ml) at −78 °C and the mixture stirred for 30 min. The iodide **133** (10 g, 31.8 mmol) in THF (50 ml) was added and the mixture stirred at −78 °C for 2.5 h. Saturated aqueous ammonium chloride (50 ml) was added and the reaction warmed to ambient temperature then diluted with ether and washed with water and brine then dried ($MgSO_4$). After concentration under reduced pressure,

chromatography of the residue using petrol : ethyl acetate (3 : 1) gave the title compound **136** (4.51 g, 42%) as a colourless oil, $[\alpha]_D$ +0.4 (c = 5.6) (Found: M^+, 340.2009. $C_{17}H_{32}N_2OSSi$ requires M, 340.2005); ν_{max}/cm^{-1} 2955, 2930, 1460, 1280, 1254, 1094, 838 and 776; δ_H (300 MHz, $CDCl_3$) 0.05 (6 H, s, 2 × CH_3Si), 0.90 [9 H, s, $SiC(CH_3)_3$], 0.96 (3 H, d, J 7, 5-CH_3), 1.45 (1 H, m, 5-H), 1.85 (2 H, m, 4-H_2), 3.44 (2 H, m, 6-H_2), 3.68 (3 H, s, NCH_3), 3.90 (1 H, m, 3-H), 4.85 (2 H, m, 1-H_2), 5.72 (1 H, m, 2-H), 6.90 (1 H, d, J 1, ArH) and 7.10 (1 H, d, J 1, ArH); δ_C (75 MHz, $CDCl_3$) −5.4, −5.3, 16.0, 17.1, 18.3, 25.9, 33.6, 33.7, 33.8, 37.3, 37.7, 51.9, 51.9, 67.6, 68.1, 115.6, 116.2, 122.6, 129.7, 138.6, 139.6, 139.9 and 140.0; m/z (EI) 340 (M^+, 5%), 95 (100); m/z (CI, NH_3) 341 (M^+ + 1, 100%).

(5*R*)-6-*tert*-Butyldimethylsilyloxy-5-methylhex-2-enyl(tributyl)stannane 137

A solution of the hex-2-en-3-yl sulfide **136** (3.42 g, 10.05 mmol), tributyltin hydride (5.4 ml, 20.1 mmol) and azobis-*iso*-butyronitrile (150 mg, 5% w/w) in degassed benzene (100 ml) was heated under reflux for 18 h. After concentration under reduced pressure, chromatography of the residue using petrol containing 0.5% triethylamine as eluent gave the title compound **137** (4.11 g, 79%) as a colourless oil, $[\alpha]_D$ +0.9 (c = 3.7, CH_2Cl_2) (Found: $M^+ - C_4H_9$, 461.2262. $C_{21}H_{45}OSi^{120}Sn$ requires M, 461.2262); ν_{max}/cm^{-1} 2956, 2928, 2856, 1463, 1255, 1094, 838 and 775; δ_H (300 MHz, $CDCl_3$) 0.10 (6 H, s, 2 × CH_3Si), 0.80–1.00 [27 H, m, 5-CH_3, $SiC(CH_3)_3$, 3 × $SnCH_2CH_2CH_2CH_3$), 1.30–1.80 (16 H, m, 5-H, 1-H_2, 4-H, 3 × $SnCH_2CH_2CH_2CH_3$), 2.12 (1 H, m, 4-H′), 3.45 (2 H, m, 6-H_2) 5.20 (1 H, m, 3-H) and 5.52 (1 H, m, 2-H); m/z (EI) 461 (M^+ − 57, 37%), 459 (M^+ − 57, 30%), 291 (40), 289 (30) and 75 (100).

(5*R*)-6-Hydroxy-5-methylhex-2-enyl(tributyl)stannane 138

Tetrabutylammonium fluoride in THF (1 M, 15.9 ml, 15.9 mmol) was added to the stannane **137** (4.11 g, 7.93 mmol) in THF (16 ml) and the solution stirred for 18 h. After concentration under reduced pressure, chromatography of the residue using petrol : ether (5 : 1 containing 1% triethylamine) gave the title compound **138** (2.54 g, 79%) as a colourless oil, a 2 : 1 mixture of (*E*)- and (*Z*)-isomers (Found: $M^+ - C_4H_9$, 347.1400. $C_{15}H_{31}O^{120}Sn$ requires M, 347.1397); ν_{max}/cm^{-1} 3334, 2956, 2925, 1462, 1377, 1038, 960 and 874; δ_H (300 MHz, $CDCl_3$) 0.85–1.00 (18 H, m, 5-CH_3, 3 × $SnCH_2CH_2CH_2CH_3$), 1.30–1.65 (13 H, m, 5-H, 3 × $SnCH_2CH_2CH_2CH_3$), 1.72 (2 H, d, J 8.5, 1-H_2), 1.80–2.15 (2 H, m, 4-H_2), 3.50 (2 H, m, 6-H_2), 5.15 (0.33 H, m, 2-H), 5.25 (0.67 H, dt, J 15, 7.5, 2-H) and 5.60 (1 H, m, 3-H); m/z (EI) 347 (M^+ − 57, 36%) 345 (M^+ − 57, 30), 291 (55), 289 (40) and 177 (100).

(1*R*,6*R*,3*Z*)-6-Methyl-1-phenylhept-3-ene-1,7-diol 141

Following the general procedure, tin(IV) bromide (1 M in DCM, 230 µl, 0.23 mmol), stannane **138** (92 mg, 0.23 mmol) in DCM (2 ml) and benzaldehyde in DCM (3 M, 76 µl, 0.23 mmol), after chromatography using ether : petrol (2 : 1 + 1% triethylamine) as eluent, gave the title compound **141** (42 mg, 84%) as a colourless oil, a 93 : 7 mixture of epimers, $[\alpha]_D$ +60 (c = 3.2) (Found: M^+ + NH_4, 238.1809. $C_{14}H_{24}NO_2$ requires M, 238.1807); ν_{max}/cm^{-1} 3346, 2955, 1494, 1454, 1035, 876, 759 and 701; δ_H (500 MHz, $CDCl_3$) major epimer **141** 0.87 (3 H, d, J 7, 6-CH_3), 1.63 (1 H, m, 6-H), 1.88 and 2.18 (each 1 H, dt, J 13, 7, 5-H), 2.35 (1 H, dt, J 15, 4, 2-H), 2.58 (1 H, dt, J 14, 8, 2-H′), 2.67 and 3.06 (each 1 H, br s, OH), 3.36 (1 H, dd, J 12, 4.5, 7-H), 3.46 (1 H, dd, J 11, 6, 7-H′), 4.65 (1 H, dd, J 9, 4, 1-H), 5.40–5.55 (2 H, m, 3-H and 4-H) and 7.22–7.32 (5 H, m, ArH); minor 1,6-*syn*-epimer **142** 2.05 (2 H, t, J 7, 5-H_2) and 4.69 (1 H, dd, J 8,5, 1-H); δ_C (75 MHz, $CDCl_3$) 17.0, 31.0, 35.7, 37.4, 66.8, 73.8, 125.8, 126.4, 127.5, 128.4, 131.3 and 144.4; m/z (CI/NH_3) 238 (M^+ + 18, 5%), 221 (M^+ + 1, 6), 220 (M^+, 22) and 203 (M^+ − 17, 100).

(1*S*,6*R*,3*Z*)-6-Methyl-1-phenylhept-3-ene-1,7-diol 142

TBAF in THF (1 M, 134 µl, 0.134 mmol) was added to the silyl ether **148** (30 mg, 0.09 mmol) in THF (1 ml) and the solution stirred for 18 h. After concentration under reduced pressure, chromatography of the residue using ether : petrol (2 : 1) as eluent, gave the title compound **142** (17 mg, 88%) as a colourless oil, $[\alpha]_D$ −48 (c = 1.7) (Found: M^+ + NH_4, 238.1809. $C_{14}H_{24}NO_2$ requires M, 238.1807); ν_{max}/cm^{-1} 3333, 2960, 1454, 1261, 1030, 799, 759 and 700; δ_H (500 MHz, $CDCl_3$) 0.88 (3 H, d, J 7, 6-CH_3), 1.68 (1 H, oct, J 7, 6-H), 2.05 (2 H, t, J 7, 5-H_2), 2.46 (1 H, dt, J 13.5, 5.5, 2-H), 2.75 (1 H, dt, J 13.5, 7, 2-H′), 3.40 (2 H, m, 7-H_2), 4.71 (1 H, dd, J 8, 4.5, 1-H), 5.40–5.60 (2 H, m, 3-H and 4-H) and 7.20–7.35 (5 H, m, ArH); δ_C (75 MHz, $CDCl_3$) 16.4, 30.6, 35.6, 37.1, 67.0, 73.8, 125.8, 126.3, 127.5, 128.4, 130.7 and 144.2; m/z (CI, NH_3) 238 (M^+ + 18, 18%), 221 (M^+ + 1, 27), 220 (M^+, 100) and 203 (M^+ − 17, 98).

(1*R*,6*R*,3*Z*)-7-*tert*-Butyldimethylsilyloxy-6-methyl-1-phenylhept-3-en-1-ol 143

tert-Butyldimethylsilyl chloride (101 mg, 0.673 mmol) was added to the alcohol **141** (148 mg, 0.673 mmol), triethylamine (103 ml, 0.74 mmol) and 4-*N*,*N*-dimethylaminopyridine (5 mg) in DCM (3 ml). The mixture was stirred for 18 h, diluted with DCM and washed with water and brine then dried ($MgSO_4$). After concentration under reduced pressure, chromatography of the residue using petrol : ether (5 : 1) as eluent, gave the title compound **143** (176 mg, 92%) as a colourless oil, $[\alpha]_D$ +32 (c = 2.0) (Found: M^+ + H, 335.2374. $C_{20}H_{35}O_2Si$ requires M, 335.2406); ν_{max}/cm^{-1} 3358, 2955, 2929, 1471, 1389, 1255, 1091, 837, 776 and 700; δ_H (300 MHz, $CDCl_3$) 0.10 (6 H, s, 2 × CH_3Si), 0.87 (3 H, d, J 6.5, 6-CH_3), 0.94 [9 H, s, $(CH_3)_3CSi$], 1.67 (1 H, m, 6-H), 1.90 (1 H, dt, J 14, 7, 5-H), 2.15 (1 H, d, J 3, OH), 2.20 (1 H, m, 5-H′), 2.55 (2 H, m, 2-H_2), 3.45 (2 H, m, 7-H_2), 4.75 (1 H, m, 1-H), 5.55 (2 H, m, 3-H and 4-H) and 7.30–7.45 (5 H, m, ArH); δ_C (75 MHz, $CDCl_3$) −5.3, 16.5, 18.4, 26.0, 31.0, 36.3, 37.4, 67.9, 73.9, 125.7, 125.9, 127.5, 128.4, 131.9 and 144.2; m/z (CI, NH_3) 335 (M^+ + 1, 5%), 334 (M^+, 2) and 317 (M^+ − 17, 100).

(1*R*,6*R*,3*Z*)-1-[(*R*)-2-Acetoxy-2-phenylacetoxy]-7-*tert*-butyldimethylsilyloxy-6-methyl-1-phenylhept-3-ene 144

Following the general procedure, alcohol **143** (27 mg, 0.081 mmol), after chromatography using petrol : ether (5 : 1) as eluent, gave the title compound **144** (37 mg, 90%) as a colourless oil, $[\alpha]_D$ −18 (c = 3.7) (Found: M^+ + NH_4, 528.3135. $C_{30}H_{46}NO_5Si$ requires M, 528.3145); ν_{max}/cm^{-1} 2955, 2929, 1751, 1372, 1207, 1175, 1085, 1059, 838, 776 and 698; δ_H (300 MHz, $CDCl_3$) 0.05 (6 H, s, 2 × CH_3Si), 0.83 (3 H, d, J 7, 6-CH_3), 0.92 [9 H, s, $SiC(CH_3)_3$], 1.60

(1 H, m, 6-H), 1.78 (1 H, dt, *J* 14.5, 7.5, 5-H), 2.10 (1 H, dt, *J* 13, 7, 5-H′), 2.22 (3 H, s, CH_3CO_2), 2.60 (2 H, m, 2-H_2), 3.40 (2 H, dd, *J* 6, 1.5, 7-H_2), 5.45 (2 H, m, 3-H and 4-H), 5.76 (1 H, t, *J* 7, 1-H), 6.01 (1 H, s, 2′-H) and 6.95–7.45 (10 H, m, ArH); δ_C (75 MHz, $CDCl_3$) −5.3, 16.4, 18.3, 20.7, 25.9, 30.8, 34.3, 36.2, 67.8, 74.5, 77.2, 124.3, 126.1, 127.7, 127.8, 127.9, 128.7, 129.2, 131.5, 133.7, 139.5, 167.9 and 170.3; *m*/*z* (CI, NH_3) 528 (M^+ + 18, 5%) and 317 (100).

(1*R*,6*R*,3*Z*)-1-[(*S*)-2-Acetoxy-2-phenylacetoxy]-7-*tert*-butyldimethylsilyloxy-6-methyl-1-phenylhept-3-ene 145

Following the general procedure, alcohol **141** (27 mg, 0.081 mmol), after chromatography using petrol : ether (5 : 1) as eluent, gave the title compound **145** (33 mg, 80%) as a colourless oil, $[\alpha]_D$ +54 (*c* = 3.3) (Found: $M^+ + NH_4$, 528.3113. $C_{30}H_{46}NO_5Si$ requires *M*, 528.3145); ν_{max}/cm^{-1} 2956, 1748, 1373, 1232, 1176, 1084, 1060, 838, 758 and 698; δ_H (300 MHz, $CDCl_3$) 0.05 (6 H, s, 2 × CH_3Si), 0.78 (3 H, d, *J* 6.5, 6-CH_3), 0.93 [9 H, s, $SiC(CH_3)_3$], 1.55 (1 H, oct, *J* 6.5, 6-H), 1.70 and 1.95 (each 1 H, dt, *J* 14, 6.5, 5-H), 2.20 (3 H, s, CH_3CO_2), 2.55 (2 H, m, 2-H_2), 3.36 (2 H, d, *J* 6, 7-H_2), 5.10 and 5.35 (each 1 H, m, 3-H or 4-H), 5.80 (1 H, t, *J* 6.5, 1-H), 6.05 (1 H, s, 2′-H) and 7.30–7.55 (10 H, m, ArH); δ_C (75 MHz, $CDCl_3$) −5.3, 16.4, 18.3, 20.7, 26.0, 29.7, 30.7, 34.1, 36.1, 67.7, 74.6, 124.2, 126.3, 127.7, 128.0, 128.4, 128.7, 129.2, 131.3, 134.0, 139.5, 168.2 and 170.2; *m*/*z* (CI, NH_3) 528 (M^+ + 18, 8%) and 317 (100).

(1*R*,6*R*,3*Z*)-1,7-diacetoxy-6-methyl-1-phenylhept-3-ene 146

Acetic anhydride (195 µl, 2.07 mmol) was added to the diol **141** (114 mg, 0.52 mmol), triethylamine (72 µl, 5.2 mmol) and 4-*N*,*N*-dimethylaminopyridine (10 mg) in DCM (5 ml) and the solution stirred for 18 h. Water was added, the aqueous phase was extracted with DCM and the organic extracts were washed with brine and dried ($MgSO_4$). After concentration under reduced pressure, chromatography using petrol : ether (4 : 1) as eluent gave the title compound **146** (141 mg, 90%) as a colourless oil, $[\alpha]_D$ +27 (*c* = 3.4); (Found: $M^+ + NH_4$, 322.2032. $C_{18}H_{28}NO_4$ requires *M*, 322.2018); ν_{max}/cm^{-1} 2962, 1739, 1373, 1237, 1035 and 701; δ_H (300 MHz, $CDCl_3$) 0.90 (3 H, d, *J* 7, 6-CH_3), 1.85 (2 H, m, 5-H_2), 2.07 and 2.11 (each 3 H, s, CH_3CO_2), 2.12 (1 H, m, 6-H), 2.55 and 2.70 (each 1 H, dt, *J* 14.5, 7.5, 2-H), 3.87 and 3.94 (each 1 H, dd, *J* 11, 6, 7-H), 5.35–5.55 (2 H, m, 3-H and 4-H), 5.79 (1 H, t, *J* 7, 1-H) and 7.30–7.40 (5 H, m, ArH); δ_C (75 MHz, $CDCl_3$) 16.6, 21.0, 21.3, 31.0, 32.9, 34.4, 68.7, 75.5, 125.6, 126.5, 128.0, 128.4, 130.2, 140.2, 170.3 and 171.2; *m*/*z* (CI, NH_3) 322 (M^+ + 18, 18%) and 245 (100).

Following the procedure outlined for the ozonolysis of acetate **11**, bis-acetate **146** (106 mg, 0.349 mmol), after chromatography using petrol : ether (5 : 2) as eluent, gave (*R*)-3-acetoxy-1-phenylpropan-1-ol (*R*)-**15** (11 mg, 16%) as a colourless oil, $[\alpha]_D$ +31 (*c* = 1), and a mixture of (*R*)-3-acetoxy-3-phenylpropan-1-ol (*R*)-**14** and (*R*)-4-acetoxy-3-methylbutan-1-ol, which were separated by reverse phase semi-preparative HPLC using acetonitrile : water (1 : 1, flow rate 15 ml min^{-1}) as eluent to give (*R*)-3-acetoxy-3-phenylpropan-1-ol (*R*)-**14**[1a] (23 mg, 34%) as a colourless oil, $[\alpha]_D$ +73 (*c* = 2), and (*R*)-4-acetoxy-3-methylbutan-1-ol (5 mg, 10%) as a colourless oil, $[\alpha]_D$ −3.5 (*c* = 0.5) (Found: $M^+ + NH_4$, 164.1285. $C_7H_{18}NO_3$ requires *M*, 164.1287); ν_{max}/cm^{-1} 3410, 2917, 1737, 1245, 1037 and 756; δ_H (300 MHz, $CDCl_3$) 1.02 (3 H, d, *J* 7, 3-CH_3), 1.40–1.75 (3 H, m, OH, 2-H_2), 2.00 (1 H, oct, *J* 7, 3-H), 2.10 (3 H, s, CH_3CO_2), 3.75 (2 H, m, 1-H_2) and 3.97 (2 H, m, 4-H_2); *m*/*z* (CI/NH_3) 164 (M^+ + 18, 100%) and 147 (M^+ + 1, 25).

(1*S*,6*R*,3*Z*)-7-*tert*-Butyldimethylsilyloxy-6-methyl-1-phenylhept-3-en-1-ol 148

Following the procedure outlined for the synthesis of 4-nitrobenzoate **86**, alcohol **143** (98 mg, 0.293 mmol), after chromatography using petrol : ether (30 : 1) as eluent, gave the inverted 4-nitrobenzoate **147** (97 mg, 69%) as a colourless oil, $[\alpha]_D$ +19.5 (*c* = 1.7); ν_{max}/cm^{-1} 2955, 1728, 1530, 1344, 1272, 1102, 838, 777 and 720; δ_H (300 MHz, $CDCl_3$) 0.05 (6 H, s, 2 × CH_3Si), 0.86 (3 H, d, *J* 7, 6-CH_3), 0.92 [9 H, s, $(CH_3)_3CSi$], 1.60 (1 H, m, 6-H), 1.86 and 2.20 (each 1 H, dd, *J* 14, 7, 5-H), 2.72 and 2.90 (each 1 H, dt, *J* 15, 7.5, 2-H), 3.41 (2 H, d, *J* 6, 7-H_2), 5.50 (2 H, m, 3-H and 4-H), 6.06 (1 H, t, *J* 7, 1-H), 7.30–7.50 (5 H, m, ArH) and 8.30 (4 H, m, ArH); δ_C (75 MHz, $CDCl_3$) −5.3, 16.5, 18.3, 25.9, 30.9, 34.4, 36.2, 67.6, 123.5, 124.4, 126.6, 128.3, 128.6, 130.8, 131.9, 135.9, 139.6, 150.6 and 163.9.

Following the procedure outlined for the synthesis of alcohol **81**, nitrobenzoate **147** (75 mg, 0.157 mmol) gave the title compound **148** (38 mg, 73%) as a colourless oil, $[\alpha]_D$ −16 (*c* = 3.7) (Found: M^+ + H, 335.2404. $C_{20}H_{35}O_2Si$ requires *M*, 335.2406); ν_{max}/cm^{-1} 3385, 2955, 2929, 1471, 1255, 1091, 837, 776 and 700; δ_H (300 MHz, $CDCl_3$) 0.05 (6 H, s, 2 × CH_3Si), 0.90 (3 H, d, *J* 7, 6-CH_3), 0.94 [9 H, s, $(CH_3)_3CSi$], 1.68 (1 H, oct, *J* 6.5, 6-H), 1.90 (1 H, dt, *J* 15, 7.5, 5-H), 2.20 (2 H, m, 5-H′ and OH), 2.55 (2 H, m, 2-H_2), 3.45 (2 H, m, 7-H_2), 4.75 (1 H, dd, *J* 7.5, 5.5, 1-H), 5.55 (2 H, m, 3-H and 4-H) and 7.30–7.45 (5 H, m, ArH); δ_C (75 MHz, $CDCl_3$) −5.3, 16.5, 18.4, 26.0, 30.9, 36.3, 37.4, 67.8, 73.9, 125.8, 125.9, 127.5, 128.4, 131.8 and 144.2; *m*/*z* (CI, NH_3) 335 (M^+ + 1, 8%), 334 (M^+, 2) and 317 (M^+ − 17, 100).

(3*RS*,6*R*)-6-*tert*-Butyldimethylsilyloxy-3-(*N*-methylimidazol-2-ylthio)hept-1-ene 161

Butyllithium in hexanes (1.6 M, 19.6 ml, 31.36 mmol) was added to the propenyl sulfide **133** (4.43 g, 28.77 mmol) in THF (150 ml) at −78 °C. After 20 min, the 3-*tert*-butyldimethylsilyloxy-1-iodobutane **160** (9.04 g, 28.79 mmol) in THF (50 ml) was added and the solution maintained at −78 °C for 2.5 h. Saturated aqueous ammonium chloride (20 ml) was added and the mixture was allowed to warm to room temperature. Water (150 ml) and ether (200 ml) were added, the aqueous phase was extracted with ether (100 ml) and the organic extracts were washed with brine (250 ml), dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography using petrol : ether (1 : 3) as eluent afforded the title compound **161** (8.09 g, 83%) as a colourless oil, a mixture of epimers, $[\alpha]_D$ +0.6 (*c* = 0.86) (Found: M^+ + H, 341.2080. $C_{17}H_{33}N_2OSSi$ requires *M*, 341.2083); ν_{max}/cm^{-1} 2955, 2930, 2857, 1458, 1255, 1131, 1078, 1047, 1005, 916, 836 and 775; δ_H (300 MHz, $CDCl_3$) 0.05 (1.5 H, s, $SiCH_3$), 0.07 (4.5 H, s, 3 × $SiCH_3$), 0.90 [9 H, s, $SiC(CH_3)_3$], 1.14 (3 H, d, *J* 6, 7-H_3), 1.45–1.90 (4 H, m, 4-H_2 and 5-H_2), 3.69 (3 H, s, NCH_3), 3.82 (2 H, m, 3-H and 6-H), 4.91 (2 H, m, 1-H_2), 5.76 (1 H, m, 2-H) and 6.95 and 7.11 (each 1 H, s, ArH); δ_C (75 MHz, $CDCl_3$) −4.7, −4.4, 18.1,

23.7, 23.9, 25.9, 30.3, 30.3, 33.8, 37.0, 37.1, 53.8, 53.8, 68.1, 68.2, 116.3, 122.6, 129.6, 138.7 and 140.1; *m/z* (CI, NH_3) 341 (M^+ + 1, 100%), 301 (14) and 115 (42).

(*R*)-6-*tert*-Butyldimethylsilyloxyhept-2-enyl(tributyl)stannane 162

Tributyltin hydride (13.85 g, 47.59 mmol) and azo-bis-*iso*-butyronitrile (390 mg, 2.38 mmol) were added to a degassed solution of the alkenyl sulfide **161** (8.09 g, 23.79 mmol) in benzene (240 ml) and the solution heated under reflux for 1.5 h. After concentration under reduced pressure, chromatography of the residue using petrol (+ 1% triethylamine) as eluent gave the title compound **162** (11.27 g, 92%) as a colourless oil, a 2 : 1 mixture of (*E*)- and (*Z*)-isomers, $[\alpha]_D$ −7.1 (*c* = 1.19) (Found: $M^+ - C_4H_9$, 461.2259. $C_{21}H_{45}OSi^{120}Sn$ requires *M*, 461.2262; ν_{max}/cm^{-1} 2957, 2928, 2856, 1463, 1254, 1133, 1083, 1035, 960, 836 and 774; δ_H (300 MHz, $CDCl_3$) 0.06 (6 H, s, 2 × $SiCH_3$), 0.82–0.97 [24 H, m, 3 × $SnCH_2CH_2CH_2CH_3$ and $SiC(CH_3)_3$], 1.16 (2 H, d, *J* 6.5, 7-H_3), 1.18 (1 H, d, *J* 6, 7-H_3), 1.25–1.80 (16 H, m, 1-H_2, 5-H_2 and 3 × $SnCH_2CH_2CH_2CH_3$), 2.02 (2 H, m, 4-H_2), 3.81 (1 H, m, 6-H) and 4.95–5.65 (2 H, m, 2-H and 3-H); δ_C (75 MHz, $CDCl_3$) −4.7, −4.3, 9.1, 9.3, 10.5, 11.2, 13.8, 14.1, 18.2, 23.5, 23.8, 25.9, 27.4, 29.0, 29.2, 39.2, 40.3, 68.3, 68.5, 124.0, 125.2, 128.3 and 129.1; *m/z* (CI, NH_3) 461 (M^+ − 57, 32%), 459 (M^+ − 57, 28), 308 (100) and 306 (65).

(*R*)-6-Hydroxyhept-2-enyl(tributyl)stannane 163

TBAF in THF (1 M, 10.3 ml, 10.30 mmol) was added to the silyl ether **162** (1.77 g, 3.42 mmol) and the solution stirred at room temperature for 50 h. Water (10 ml) was added, the mixture was stirred for 1 h, then extracted with ether (4 × 15 ml). The organic extracts were washed with brine (50 ml), dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the residue using petrol : ether (2 : 1 + 1% triethylamine) as eluent gave the title compound **163** (1.10 g, 80%) as a colourless oil, a 2 : 1 mixture of (*E*)- and (*Z*)-isomers, $[\alpha]_D$ −3.4 (*c* = 1.08) (Found: $M^+ - C_4H_9$, 347.1397. $C_{15}H_{31}O^{120}Sn$ requires *M*, 347.1397); ν_{max}/cm^{-1} 3331, 2957, 2925, 2872, 1463, 1376, 1075 and 960; δ_H (300 Mz, $CDCl_3$) 0.85–1.00 (15 H, m, 3 × $SnCH_2CH_2CH_2CH_3$), 1.21 (2 H, d, *J* 6, 7-H_3), 1.24 (1 H, d, *J* 6, 7-H_3), 1.26–1.80 (16 H, m, 3 × $SnCH_2CH_2CH_2CH_3$, 1-H_2 and 4-H_2), 2.10 (2 H, m, 5-H_2), 3.85 (1 H, m, 6-H), 5.11 (0.33 H, dt, *J* 10.5, 7, 2- or 3-H), 5.25 (0.67 H, dt, *J* 15, 7, 2- or 3-H) and 5.60 (1 H, m, 2- or 3-H); δ_C (75 MHz, $CDCl_3$) 9.1, 9.4, 10.5, 11.2, 13.8, 14.2, 23.4, 27.4, 29.2, 39.2, 39.6, 67.9, 68.2, 123.5, 124.9, 129.1 and 129.9; *m/z* (EI) 347 (M^+ − 57, 72%), 345 (M^+ − 57, 55), 291 (39), 289 (40) and 233 (15).

(1*S*,7*R*,3*Z*)-1-Phenyloct-3-ene-1,7-diol 164

Following the general procedure, stannane **163** (500 mg, 1.24 mmol), tin(IV) bromide (545 mg, 1.24 mmol) in DCM (1 ml) and benzaldehyde (132 mg, 1.24 mmol) in DCM (0.5 ml), after chromatography using petrol : ether (1 : 2 + 1% triethylamine) as eluent gave the title compound **164** (196 mg, 72%) as a colourless oil, a 92 : 8 mixture of epimers, $[\alpha]_D$ −71 (*c* = 0.82) (Found: M+, 220.1456. $C_{14}H_{20}O_2$ requires *M*, 220.1463); ν_{max}/cm^{-1} 3348, 2965, 2925, 1453, 1129, 1081, 1053, 759 and 701; δ_H (500 MHz, $CDCl_3$) 1.12 (3 H, d, *J* 6, 8-H_3), 1.41 (2 H, m, 6-H_2), 2.10 (4 H, m, 2- or 5-H_2 and 2 × OH), 2.51 (2 H, t, *J* 7, 2- or 5-H_2), 3.73 (1 H, m, 7-H), 4.72 (1 H, t, *J* 6, 1-H), 5.35 and 5.51 (each 1 H, dt, *J* 10.5, 7, 3-H or 4-H) and 7.24–7.32 (5 H, m, ArH); δ_C (75 MHz, $CDCl_3$) major epimer **164** 23.6, 23.9, 37.1, 38.6, 67.5, 73.7, 125.1, 125.9, 127.4, 128.4, 133.0 and 144.1; minor 1,7-*anti*-epimer 37.4 and 38.4; *m/z* (CI, NH_3) 221 (M^+ + 1, 35%), 204 (100) and 186 (85).

(1*R*,7*R*,3*Z*)-1-Phenyloct-3-ene-1,7-diol 165

TBAF in THF (1 M, 0.74 ml, 0.74 mmol) was added to the silyl ether **171** (82 mg, 0.246 mmol) in THF (0.3 ml) and the solution stirred at room temperature for 72 h. Water (2 ml) was added and the mixture stirred for 1 h, then extracted with ether (4 × 5 ml). The organic extracts were washed with brine (10 ml), dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the residue using petrol : ethyl acetate (1 : 1) as eluent gave the title compound **165** (52 mg, 96%) as a colourless oil, $[\alpha]_D$ +58 (*c* = 2.22) (Found: M^+, 220.1462. $C_{14}H_{20}O_2$ requires *M*, 220.1463); ν_{max}/cm^{-1} 3358, 2965, 2924, 1453, 1130, 1081, 1054, 759 and 700; δ_H (500 MHz, $CDCl_3$) 1.11 (3 H, d, *J* 6.5, 8-H_3), 1.41 (2 H, m, 6-H_2), 2.00 and 2.24 (each 1 H, m, 2- or 5-H), 2.34 (1 H, dt, *J* 14, 5, 2- or 5-H), 2.58 (1 H, dt, *J* 14, 8, 2- or 5-H), 2.82 (2 H, br s, 2 × OH), 3.72 (1 H, m, 7-H), 4.63 (1 H, dd, *J* 8.5, 4, 1-H), 5.44 (2 H, m, 3-H and 4-H) and 7.21–7.34 (5 H, m, ArH); δ_C (75 MHz, $CDCl_3$) major 1,6-*anti*-epimer **165** 23.5, 37.4, 38.3, 66.6, 73.7, 125.6, 125.7, 127.4, 128.2, 132.3 and 144.3; minor 1,7-*syn*-epimer **164** 23.6, 37.1 and 38.6; *m/z* (CI, NH_3) 238 (M^+ + 18, 12%), 220 (M^+, 38), 203 (M^+ − 17, 100) and 185 (87).

(1*S*,7*R*,3*Z*)-7-*tert*-Butyldimethylsilyloxy-1-phenyloct-3-en-1-ol 166, (2*R*,8*S*,5*Z*)-8-*tert*-butyldimethylsilyloxy-8-phenyloct-5-en-2-ol 167 and (1*S*,7*R*,3*Z*)-1,7-bis-(*tert*-butyldimethylsilyloxy)-1-phenyloct-3-ene 168

Imidazole (78 mg, 1.15 mmol) and *tert*-butyldimethylsilyl chloride (173 mg, 1.15 mmol) were added to the diol **164** (230 mg, 1.045 mmol) in *N*,*N*-dimethylformamide (1 ml) and the mixture stirred at room temperature for 15 h. Water (2 ml) was added and the mixture extracted with ether (4 × 10 ml). The organic extracts were washed with brine (30 ml), dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the residue using petrol : ether (7 : 1 to 1 : 3) as eluent afforded the title compound **168** (72 mg, 15%) as a colourless oil, $[\alpha]_D$ −25 (*c* = 1.12) (Found: M^+ − H, 447.3117. $C_{26}H_{47}O_2Si_2$ requires *M*, 447.3115); ν_{max}/cm^{-1} 2957, 2929, 2858, 1472, 1382, 1255, 1137, 1091, 836 and 775; δ_H (300 MHz, $CDCl_3$) −0.07, 0.07, 0.08 and 0.09 (each 3 H, s, $SiCH_3$), 0.92 and 0.93 [each 9 H, s, $SiC(CH_3)_3$], 1.13 (3 H, d, *J* 6, 8-H_3), 1.25–1.55 (2 H, m, 6-H_2), 1.85–2.18 and 2.45 (each 2 H, m, 2-H_2 or 5-H_2), 3.78 (1 H, m, 7-H), 4.70 (1 H, t, *J* 6, 1-H), 5.44 (2 H, m, 3-H and 4-H) and 7.21–7.36 (5 H, m, ArH); δ_C (75 MHz, $CDCl_3$) −4.9, −4.7, −4.3, 18.2, 18.3, 23.7, 23.8, 25.9, 25.9, 38.9, 39.6, 68.3, 75.1, 125.7, 126.0, 126.7, 127.9, 131.5 and 145.3; *m/z* (FAB, Xe) 447 (M^+ − 1, 1%), 433 (2), 315 (6) and 221 (100). The second fraction contained the title compound **166** (219 mg, 63%) as a colourless oil, $[\alpha]_D$ −61 (*c* = 0.88) (Found: M^+ − OH, 317.2295. $C_{20}H_{33}OSi$ requires *M*, 317.2301); ν_{max}/cm^{-1} 3365, 2957, 2929, 2857, 1255, 1137, 1091, 1051, 1005, 836, 775 and 700; δ_H (500 MHz, $CDCl_3$) 0.09 (6 H, s, 2 × $SiCH_3$), 0.94 [9 H, s, $SiC(CH_3)_3$], 1.15 (3 H, d, *J* 6, 8-H_3), 1.43 (2 H, m, 6-H_2), 1.95–2.25 (2 H, m, 2- or 5-H_2), 1.98 (1 H, d, *J* 2.5,

OH), 2.57 (2 H, m, 2- or 5-H_2), 3.82 (1 H, m, 7-H), 4.74 (1 H, ddd, *J* 7.5, 5.5, 2.5, 1-H), 5.43 and 5.60 (each 1 H, m, 3-H or 4-H) and 7.28–7.44 (5 H, m, ArH); δ_C (75 MHz, $CDCl_3$) –4.7, –4.3, 18.2, 23.7, 23.8, 25.9, 37.3, 39.5, 68.3, 73.9, 124.7, 125.9, 127.5, 128.4, 133.4 and 144.1; *m/z* (CI, NH_3) 317 (M^+ – 17, 78%), 221 (70), 185 (100) and 143 (75). The third fraction contained the title compound **167** (18 mg, 5%) as a colourless oil, $[\alpha]_D$ –29 (*c* = 0.52) (Found: M^+ – OH, 317.2310. $C_{20}H_{33}OSi$ requires *M*, 317.2301); ν_{max}/cm^{-1} 3333, 2957, 2929, 2857, 1255, 1088, 1070, 836, 777 and 700; δ_H (300 MHz, $CDCl_3$) –0.08 and 0.06 (each 3 H, s, $SiCH_3$), 0.93 [9 H, s, $SiC(CH_3)_3$], 1.18 (3 H, d, *J* 6, 8-H_3), 1.28 (1 H, d, *J* 5, OH), 1.40 (2 H, m, 6-H_2), 2.04 and 2.49 (each 2 H, m, 2-H_2 or 5-H_2), 3.73 (1 H, m, 7-H), 4.71 (1 H, t, *J* 6, 1-H), 5.46 (2 H, m, 3-H and 4-H) and 7.20–7.35 (5 H, m, ArH); δ_C (75 MHz, $CDCl_3$) –4.9, –4.7, 18.3, 23.5, 23.7, 25.9, 38.9, 67.7, 75.0, 126.0, 126.2, 126.9, 127.9, 131.1 and 145.3; *m/z* (CI, NH_3) 335 (M^+ + 1, 1%), 317 (M^+ – 17, 8), 220 (75), 203 (85), 185 (60) and 102 (100). The fourth fraction contained recovered starting material **164** (33 mg, 14%).

(1*S*,7*R*,3*Z*)-1,7-Diacetoxy-1-phenyloct-3-ene 169

Triethylamine (500 mg, 4.95 mmol), 4-*N*,*N*-dimethylaminopyridine (6 mg, 0.049 mmol) and acetic anhydride (202 mg, 1.98 mmol) were added to the diol **164** (109 mg, 0.495 mmol) in DCM (3 ml) and the solution stirred at room temperature for 15 h. DCM (35 ml) and water (35 ml) were added, and the organic phase washed with aqueous hydrogen chloride (3.5 M, 25 ml), saturated aqueous sodium hydrogen carbonate (25 ml) and brine (15 ml) then dried ($MgSO_4$). After concentration under reduced pressure, chromatography of the residue using petrol : ether (3 : 1) as eluent gave the title compound **169** (145 mg, 96%) as a colourless oil, $[\alpha]_D$ –39 (*c* = 1.10) (Found $M^+ + NH_4$, 322.2021. $C_{18}H_{28}NO_4$ requires *M*, 332.2018); ν_{max}/cm^{-1} 2937, 1736, 1373, 1238, 1024 and 701; δ_H (300 MHz, $CDCl_3$) 1.22 (3 H, d, *J* 6.5, 8-H_3), 1.33–1.68 (2 H, m, 6-H_2), 2.01 (2 H, m, 2- or 5-H_2), 2.05 and 2.10 (each 3 H, s, CH_3CO_2), 2.54 and 2.68 (each 1 H, dt, *J* 14.5, 7, 2- or 5-H), 4.87 (1 H, m, 7-H), 5.36 and 5.47 (each 1 H, dt, *J* 10.5, 7, 3-H or 4-H), 5.77 (1 H, t, *J* 6.5, 1-H) and 7.28–7.40 (5 H, m, ArH); δ_C (75 MHz, $CDCl_3$) 19.9, 21.3, 21.4, 23.4, 34.3, 35.6, 70.5, 75.5, 124.5, 126.6, 127.9, 128.4, 131.9, 140.2, 170.2 and 170.7; *m/z* (CI, NH_3) 322 M^+ + 18, 1%), 245 (26) and 185 (100).

Ozone was bubbled through a solution of the alkene **169** (107 mg, 0.352 mmol) in DCM (5 ml) at –78 °C for 15 min. The solution was purged with oxygen for 10 min, then dimethyl sulfide (200 mg, 3.23 mmol) was added and the solution allowed to warm to room temperature. After concentration under reduced pressure, the residue was dissolved in DCM (2 ml) and methanol (2 ml) and sodium borohydride (82 mg, 2.16 mmol) were added at 0 °C. After 15 min at room temperature, aqueous hydrogen chloride (1 M, 2 ml) was added at 0 °C. After warming to room temperature DCM (25 ml) and water (25 ml) were added, and the aqueous phase was extracted with DCM (25 ml). The organic extracts were washed with brine (30 ml), dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the residue using petrol : ether (2 : 1) gave (*S*)-3-acetoxy-1-phenylpropan-1-ol (*S*)-**15** (9 mg, 13%) as a colourless oil, $[\alpha]_D$ –25 (*c* = 0.73) and a 3 : 1 mixture of (*S*)-3-acetoxy-3-phenylpropan-1-ol (*S*)-**14** and (*R*)-4-acetoxypent-1-ol (58 mg). HPLC of this mixture allowed the isolation of (*S*)-3-acetoxy-3-phenylpropan-1-ol (*S*)-**14** (18 mg, 27%) as a colourless oil, $[\alpha]_D$ –72 (*c* = 0.92)[1a] with spectroscopic data identical to those of a sample prepared earlier.

(1*R*,7*R*,3*Z*)-7-*tert*-Butyldimethylsilyloxy-1-phenyloct-3-en-1-yl 4-nitrobenzoate 170

Diethyl azodicarboxylate (149 mg, 0.856 mmol) was added to a suspension of alcohol **166** (190 mg, 0.569 mmol), triphenylphosphine (223 mg, 0.853 mmol) and 4-nitrobenzoic acid (142 mg, 0.853 mmol) in toluene (4.5 ml) at –35 °C and the mixture was allowed to warm to room temperature. After 2 h, ether (30 ml) and water (30 ml) were added and the organic phase was washed with brine (30 ml) and dried ($MgSO_4$). Concentration under reduced pressure gave a solid which was absorbed onto silica. Chromatography using petrol : ether (10 : 1) as eluent afforded the title compound **170** (203 mg, 74%) as a colourless oil, $[\alpha]_D$ –30 (*c* = 1.39) (Found: M^+ – H, 482.2370. $C_{27}H_{36}NO_5Si$ requires *M*, 482.2363); ν_{max}/cm^{-1} 2929, 2856, 1727, 1608, 1530, 1344, 1272, 1102, 837, 775 and 720; δ_H (300 MHz, $CDCl_3$) 0.08 and 0.09 (each 3 H, s, $SiCH_3$), 0.92 [9 H, s, $SiC(CH_3)_3$], 1.13 (3 H, d, *J* 6, 8-H_3), 1.40 (2 H, m, 6-H_2), 1.90–2.25 (2 H, m, 2- or 5-H_2), 2.74 and 2.90 (each 1 H, dt, *J* 14.5, 7, 2- or 5-H), 3.79 (1 H, m, 7-H), 5.39 and 5.55 (each 1 H, dt, *J* 10.5, 7.5, 3-H or 4-H), 6.07 (1 H, t, *J* 7, 1-H), 7.30–7.50 (5 H, m, ArH) and 8.22–8.37 (4 H, m, ArH); δ_C (75 MHz, $CDCl_3$), –4.7, –4.3, 18.1, 23.8, 25.9, 34.3, 39.4, 68.2, 77.4, 123.3, 123.6, 126.6, 128.3, 128.6, 130.8, 133.4, 135.9, 139.6, 150.6 and 163.9; *m/z* (FAB, Xe) 482 (M^+ – 1, 2%), 317 (26), 221 (100), 185 (64), 143 (84), 129 (83) and 115 (80).

(1*R*,7*R*,3*Z*)-7-*tert*-Butyldimethylsilyloxy-1-phenyloct-3-en-1-ol 171

Sodium hydroxide (101 mg, 2.53 mmol) was added to the ester **170** (175 mg, 0.362 mmol) in methanol (10 ml) and, after 2 h at room temperature, water (15 ml) was added. The mixture was extracted with ether (2 × 20 ml) and the organic extracts were washed with brine (30 ml), dried ($MgSO_4$) and concentrated under reduced pressure to afford the title compound **171** (112 mg, 93%) as a colourless oil, $[\alpha]_D$ +15 (*c* = 0.98) (Found: M^+ – OH, 317.2305. $C_{20}H_{33}OSi$ requires *M*, 317.2301); ν_{max}/cm^{-1} 3359, 2957, 2929, 2857, 1255, 1137, 1091, 1051, 1001, 836, 775 and 700; δ_H (300 MHz, $CDCl_3$) 0.11 (6 H, s, 2 × $Si(CH_3)$), 0.95 [9 H, s, $SiC(CH_3)_3$], 1.16 (3 H, d, *J* 6, 8-H_3), 1.45 (2 H, m, 6-H_2), 1.90–2.25 (3 H, m, 2- or 5-H_2 and OH), 2.55 (2 H, m, 2- or 5-H_2), 3.82 (1 H, m, 7-H), 4.75 (1 H, dd, *J* 7.5, 5.5, 1-H), 5.43 and 5.61 (each 1 H, m, 3-H or 4-H) and 7.26–7.42 (5 H, m, ArH); δ_C (75 MHz, $CDCl_3$) –4.7, –4.3, 18.2, 23.7, 23.8, 25.9, 37.4, 39.5, 68.3, 74.0, 124.8, 125.9, 127.5, 128.4, 133.5 and 144.1; *m/z* (CI, NH_3) 317 (M^+ – 17, 100%), 221 (51) and 185 (68).

(1*S*,7*R*,3*Z*)-1-[(*R*)-2-Acetoxy-2-phenylacetoxy]-7-*tert*-butyldimethylsilyloxy-1-phenyloct-3-ene 172

Following the general procedure, alcohol **166** (25 mg, 0.075 mmol) and (*R*)-2-acetoxy-2-phenylacetic acid, after chromatography using petrol : ether (4 : 1) as eluent, gave the title compound **172** (30 mg, 78%) as a colourless oil, $[\alpha]_D$ –61 (*c* = 1.36) (Found: $M^+ + NH_4$, 528.3142. $C_{30}H_{46}NO_5Si$ requires *M*, 528.3145); ν_{max}/cm^{-1} 2929, 1750, 1373, 1231, 1208, 1174, 1138, 1084, 1058, 1003, 836, 775 and 698; δ_H (300 MHz, $CDCl_3$) 0.06 and 0.08 (each 3 H, s,

$SiCH_3$), 0.92 [9 H, s, $SiC(CH_3)_3$], 1.10 (3 H, d, *J* 6, 8-H_3), 1.17–1.44 (2 H, m, 6-H_2), 1.73–2.01 (2 H, m, 2- or 5-H_2), 2.21 (3 H, s, CH_3CO_2), 2.42–2.65 (2 H, m, 2- or 5-H_2), 3.73 (1 H, m, 7-H), 5.06 and 5.33 (each 1 H, m, 3-H or 4-H), 5.80 (1 H, t, *J* 7, 1-H), 6.03 (1 H, s, 2′-H) and 7.30–7.56 (10 H, m, ArH); *m*/*z* (CI, NH_3) 528 (M^+ + 18, 28%), 384 (25) and 317 (100).

(1*S*,7*R*,3*Z*)-1-[(*S*)-2-Acetoxy-2-phenylacetoxy]-7-*tert*-butyldimethylsilyloxy-1-phenyloct-3-ene 173

Following the general procedure, alcohol **166** (26 mg, 0.078 mmol) and (*S*)-2-acetoxy-2-phenylacetic acid, after chromatography using petrol : ether (4 : 1) as eluent, gave the title compound **173** (33 mg, 83%) as a colourless oil, $[\alpha]_D$ +11.5 (*c* = 1.38) (Found: M^+ + NH_4, 528.3142. $C_{30}H_{46}NO_5Si$ requires *M*, 528.3145); ν_{max}/cm^{-1} 2929, 1750, 1373, 1232, 1207, 1175, 1138, 1084, 1058, 836, 775 and 698; δ_H (300 MHz, $CDCl_3$) 0.07 and 0.09 (each 3 H, s, $SiCH_3$), 0.92 [9 H, s, $SiC(CH_3)_3$], 1.13 (3 H, d, *J* 6, 8-H_3), 1.24–1.51 (2 H, m, 6-H_2), 1.81–2.15 (2 H, m, 2- or 5-H_2), 2.22 (3 H, s, CH_3CO_2), 2.57 and 2.68 (each 1 H, dt, *J* 14.5, 7, 2- or 5-H), 3.77 (1 H, m, 7-H), 5.33 and 5.51 (each 1 H, m, 3-H or 4-H), 5.88 (1 H, t, *J* 7, 1-H), 6.05 (1 H, s, 2′-H) and 6.99–7.46 (10 H, m, ArH); *m*/*z* (CI, NH_3) 528 (M^+ + 18, 100%), 414 (28) and 317 (73).

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